



IMPERIAL AGRICULTURAL  
RESEARCH INSTITUTE, NEW DELHI.

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# PROCEEDINGS

## OF THE

### NATIONAL INSTITUTE OF SCIENCES OF INDIA

Vol. IX, No. 1, pp. 1-236

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PUBLISHED BY THE NATIONAL INSTITUTE OF SCIENCES OF INDIA

PRICE SEVEN RUPEES

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M.M., F G S, F R S, F R A S B, Bristol

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F R A S B, Benares

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Prof P Râv, M A, Calcutta

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Brevet-Col Sir R N Chopra, Kt, O I E, M D, Sc D,  
F R C P, F R A S B, I M S (Retd), Jammu Tawi

Sir Lewis Fermor, Kt, O B E, D Sc, A R S M., M.Inst.-  
M M, F G S, F R S, F R A S B, Bristol

Dr B Prashad, O B E, D Sc, F R S E, F L S, F Z S,  
F R A S B Benares

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Prof P C Mahalanobis, O B E, M A, B Sc, I E S, Calcutta.

Rai Sahib P L Srivastava, M A, D Phil, Allahabad.





## **Eighth Annual General Meeting.**

The Eighth Annual General Meeting of the National Institute of Sciences of India was held at 3-30 p m on Friday, the 1st January, 1943, in the Pure Chemistry Lecture Theatre of the University College of Science, 92 Upper Circular Road, Calcutta

The following Fellows were present —

Prof J N Mukherjee, *Vice President, in the Chair*  
Mr D. N Wadia, *Additional Vice-President*  
Mr W D West,                   "                   "  
Rai Bahadur Dr S L Hora, *Editor of Publications*  
Prof S P Agharkar, *Honorary Secretary*

Rai Bahadur Dr. K N Bagchi	Prof B B Ray
Dr J K Basu	Prof P Ray
Mr R C Bose	Dr. P B Sarkar
Dr J A Dunn	Principal J M Sen
Prof J Ghosh	Dr S C Sirkar
Dr R B Lal	Dr A C Ukil

Mr. E T Vachell

The meeting was attended also by visitors

In the unavoidable absence of the President, Dr B Prashad, Prof J N Mukherjee, one of the Vice-Presidents, took the Chair

1 The minutes of the Eighteenth Ordinary General Meeting, held on the 5th October, 1942, were read and confirmed

2 The following Ordinary Fellows signed the duplicate Obligation and were admitted as Fellows as per Rule 13 —

Dr. J K. Basu.  
Mr R C Bose  
Mr. E T Vachell

3 The Chairman appointed Principal J M Sen and Mr W D West to act as scrutineers of the ballot papers received for the election of Officers and Members of Council for the year 1943.

The following were declared elected Officers and Members of Council for the year 1943:—

*President* Dr J. C Ghosh, Bangalore  
*Vice-Presidents* Prof S K Mitra, Calcutta  
Mr D. N Wadia, Colombo.  
*Treasurer* Rai Bahadur Dr K N. Bagchi, Calcutta  
*Foreign Secretary* Prof J N Mukherjee, Calcutta  
*Secretaries* : Prof. S. P Agharkar, Calcutta.  
Dr. C S Fox, Calcutta

*Editor of Publications* Rai Bahadur Dr S L Hora, Calcutta

*Members of Council* Dr K Bagechee, Dohra Dun, Sir S S Bhatnagar, Delhi, Dr F H Gravel, Kodaikanal, Prof B C Guha, Calcutta, Dr B S Guha, Benares, Dr M Ishaq, Aligarh, Dr D S Kothari, Delhi, Prof K G Naik Baroda, Prof V V Narlikar Benares, Principal P Parja, Cuttack, Dr F G Percival, Jamshedpur, Dr K R Ramanathan, Poona, Mr B Rama Rao Bangalore, Prof P Ray, Calcutta, Prof M R Siddiqi Hyderabad Dn., Dr N K Sinha Calcutta, Dr K Venkataraman, Bombay

4 The Annual Report for the year 1942, prepared by the Council, together with the audited statement of accounts and budget estimates of income and expenditure for the year 1943, which was read out by the Honorary Secretary, was approved

5 At the request from the Chair the Honorary Secretary read out the Annual Address of the President, Dr B Prashad, entitled 'Conservation of wild life in India'

6 The Chairman moved that the felicitations of the National Institute be offered to Dr J C Ghosh who had been elected to be President for the year 1943 and on whom the honour of Knighthood had been conferred, and to Rao Bahadur B Viswanath who had received the C I E in the new year's Honours list

The resolution was passed with acclamation

With a vote of thanks to the Chair the meeting terminated

# National Institute of Sciences of India

## ANNUAL REPORT

The Council of the National Institute of Sciences of India have pleasure in submitting the following report on the general concerns of the Institute for the year 1942, as required by the provisions of Rule 48(f)

### *Membership*

The number of Fellows on the roll of the Institute at the beginning of the year was 179 Ordinary Fellows and 23 Honorary Fellows. Thirteen Ordinary Fellows were elected during the year in accordance with the procedure laid down in the Regulations. One Ordinary Fellow resigned, and one Ordinary Fellow and one Honorary Fellow died during the year. The total number of Fellows on the roll at the end of the year is 190 Ordinary Fellows and 22 Honorary Fellows. Of the 190 Ordinary Fellows 8 are non-resident.

### *Meetings*

The Seventh Annual General Meeting was held in the Central Hall of the Baroda College, Baroda, on the 1st January, 1942. An account of the meeting was published in the *Proceedings*, Vol. VIII, No. 1, pp. 5-7.

Owing to troublous situation of the country it was not possible to arrange many Ordinary General Meetings for discussion during the year. Only one meeting was held in the rooms of the Royal Asiatic Society of Bengal, 1 Park Street, Calcutta, on the 5th October, 1942. Some of the papers read at this meeting have already been published in the *Proceedings*, Vol. VIII, No. 3 and the rest are in course of publication.

### *The Council*

The officers and members of Council for the year 1942 were elected at the Seventh Annual Meeting held on the 1st January, 1942. The Council, together with the representatives of the co-operating Academies, the Indian Science Congress Association and the Government of India, was constituted as follows —

*President*

*Vice-Presidents*

*Additional Vice-Presidents*

Dr. Balmi Prasad

Prof. J. N. Mukherjee

Dr. C. W. B. Normand

Prof. K. S. Krishnan

H. R. Mohra

Mr. D. N. Wadia

Mr. W. D. West

<i>Treasurer</i>	Dr. B S Guha
<i>Foreign Secretary</i>	Dr J C Ghosh
<i>Secretaries</i>	Prof S P Agharkar Dr C S Fox
<i>Editor of Publications</i>	Rai Bahadur Dr S L Hora
<i>Members of Council</i>	Rai Bahadur Dr K N Bagchi Sir S S Bhatnagar Dr F H Gravely Dr M Ishaq Dr D S Kothari Dr M S Krishnan Prof G Matthai Prof V V Narhkar Principal G R Paranjpe Principal P Parja Dr F G Percival Prof M Qureshi Dr K R Ramanathan Rao Bahadur G N Rangaswami Ayyangar Prof M R Siddiqui Dr N K Sur Mr F Ware Brevet Col Sir R N Chopra Sir Lewis Fermor Prof M N Saha
<i>Additional Members of Council</i>	Dr D M Bose Prof P C Mahalanobis Prof S K Mitra Rai Sahib Dr P L Srivastava

} *Ex officio*

Dr B S Guha resigned his appointment of Treasurer on the 21st July, 1942, owing to transfer of his office outside Calcutta Prof J N Mukherjee, a Vice-President of the Institute, was appointed to act as Treasurer in place of Dr B S Guha

The Council held five ordinary meetings during the year Finding it difficult to obtain a quorum for a meeting during the prevailing disturbances in the country, the Council's proposal for appointing a committee consisting of the two Honorary Secretaries, Treasurer and Rai Bahadur Dr S L Hora to act on behalf of the Council in consultation with the President was approved at the Ordinary General Meeting held on the 5th October, 1942 This Committee met thrice during the year.

### *Committees*

The Sectional Committees are given in Appendix III

### *Publications*

Three numbers of the *Proceedings* and two numbers of the *Transactions* were published during the year

In a circular letter on the subject of economy of paper issued during the year the Government of India suggested that Associations might discontinue certain periodical publications during the period of the war and revise their publication programme

The Council considered the situation carefully and have decided that it was not desirable to curtail the printing of the *Proceedings*, which in these days have become one of the chief means of scientific communications. They, however, agreed to suspend the publication of the *Indian Science Abstracts* after completing the volumes for 1938 and 1939 which are in the press. The printing of these could not be completed during the year owing to various technical difficulties. The *Indian Science Abstracts* for the subsequent years will, however, be prepared and kept in typescript in the office of the Institute, with a view to future publication. It is proposed to earmark funds for this purpose. The whole question will be carefully considered at a later date.

### *Exchanges*

Three additional Institutions were placed on the distribution list for the publications of the Institute bringing the total number on the list to ninety-eight.

### *Library*

Two hundred and seventy-three parts of periodicals and reprints were added to the library during the year.

### *Presents and Donations*

The following grants-in-aid were made to the Institute during the year —

- (1) Rs 500 from the Calcutta University
- (2) Rs 300 from the Osmania University
- (3) Rs 200 from the Dacca University

The Government of India made their ordinary grant of Rs 6,000 to the Institute and expressed their inability to give the enhanced grant of Rs 7,000 for the year. A grant of Rs 500 was received from the Panjab University in connection with the printing of a paper by Dr. Vishwa Nath in the *Transactions* of the Institute.

### *Finance*

An audited statement of accounts of the Institute for the period from 1st December, 1941 to 30th November, 1942, is submitted (*vide* Appendix IV). The total ordinary receipts for this period are Rs 15,617-2-0 (inclusive of the Government of India grant of Rs 6,000) and the ordinary payments are Rs 12,161-13-9, leaving a balance of Rs 3,435-4-3. A further sum of Rs 160-0-0 was realized on account of admission fees.

A statement, showing the donations, other than recurring annual grants-in-aid, together with compounding fees and admission fees received and their investments since 1935, is given in Appendix V.

At the beginning of the year the cash position of the Institute was as follows —

	Rs	A	P
In Savings Bank account	5,713	9	0
„ Government paper	40,000	0	0
„ Current account	4,818	12	9
„ hand	14	3	0
<b>TOTAL</b>	<b>50,546</b>	<b>8</b>	<b>9</b>

At the end of the year, however, the cash position was as shown below —

	Rs	A	P
In Savings Bank account	5,757	4	0*
„ Government paper	40,000	0	0
„ Current account	8,383	8	6
„ hand	1	0	6
<b>TOTAL</b>	<b>54,141</b>	<b>12</b>	<b>0</b>

#### APPENDICES

- I List of Fellows
- II Abstract Proceedings of the Council
- III Committees, 1943
- IV Audited statement of accounts, Dec 1941–Nov 1942
- V Statement showing donations etc received and investments
- VI Budget Estimates, Dec 1942–Nov 1943

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\* Includes a sum of Rs 3,275-0-8 on account of the Permanent Fund

## APPENDIX I

### LIST OF FELLOWS.

#### ORDINARY FELLOWS

- 1 ABRAHAM, LT COL W E V, A R C S (I), F G S, M Inst P T, Senior Geologist  
Burmah Oil Co, Ltd, Burma, Khodaung, Magwe, Burma (1936)
- 2 AGHARKAR, S P, M A, Ph D, F L S, Ghose Professor of Botany, Calcutta  
University, 35 Ballygunge Circular Road, Calcutta
- 3 AHMAD, NAZIR, O B E, M Sc, Ph D, Director, Indian Central Cotton Committee's  
Technological Laboratory, Matunga, Bombay
- 4 AIYAR, R GOPALA, M A, L T, M Sc, University Professor of Zoology and Director,  
University Zoological Laboratory, Madras (1938)
- 5 AJREKAR, S L, B A, I E S (Retd), Bhandarkar Institute Road, Poona 4
- 6 ANANDA RAO, K, Rao Bahadur, M A, I E S, Professor of Mathematics, Presidency  
College, Madras
- 7 ASH W C, B.Sc., M Inst C E, A M I Mech E, Bengal Club, Calcutta
- 8 AUDEN, J B, M A (Cantab), Geologist, Geological Survey of India, Indian Museum,  
Calcutta (1938)
- 9 AWATI, P R, B A, D I C, I E S, Professor of Zoology, Royal Institute of Science,  
Mauvo Road, Bombay 1
- 10 BAGCHER K D, D Sc, D I C Mycologist Imperial Forest Research Institute,  
Dehra Dun, U P
- 11 BAGCHI, K N, Rai Bahadur, B Sc, M B, D T M, F I C, Chemical Examiner to the  
Government of Bengal and Professor of Chemistry, Calcutta Medical College,  
Calcutta (1940)
- 12 BAKL, K N, D Sc, D Phil, Professor of Zoology, Lucknow University, Lucknow
- 13 BANERJEE, K, D Sc, Reader in Physics, Dacca University, Ramna, Dacca (1939)
- 14 BANERJI, A C, M Sc, M A, F R A S, I E S, Professor of Mathematics, Allahabad  
University, Allahabad
- 15 BANERJI, S K, D Sc, Director, Upper Air Observatory, Lodi Road, New Delhi
- 16 BARDHAN, J C, D Sc (Cal & Lond.), Lecturer in Chemistry, Calcutta University,  
92 Upper Circular Road, Calcutta (1942)
- 17 BASU, J K, M Sc, Ph D, Soil Physicist, Sugarcane Research Institute, Padgaon,  
P O Nira R S, Dt Poona (1941).
- 18 BEESON, C F C., C.I.E., D Sc, Thames House, near Eynsham, Oxford
- 19 BEHARI, RAM, M A, Ph D, Reader in Mathematics, Delhi University and Professor,  
St Stephen's College, Delhi (1941)
- 20 BHABHA, H J, Ph D, F R S, Visiting Professor, Indian Institute of Science,  
Bangalore, Mehraur, Little Gibbs Road, Malabar Hill, Bombay (1941)
- 21 BHARADWAJ, Y, M Sc, Ph D (Lond), F L S, Professor of Botany and Head of  
the Department, Benares Hindu University, Benares (1937).
- 22 BHARUCHA, F R, B A, B.Sc., M Sc, D Sc, Professor of Botany and Head of the  
Department, Royal Institute of Science, Bombay (1939).
- 23 BHASKARA SHASTRI, T P, Rai Sahab, M A, F R A S, Director, Nizamiah Observa-  
tory, Hyderabad (Deccan)
- 24 BHATTAGAR, SIB S S, Kt. O B E, D.Sc., F I.C., F Inst P, Director of Scientific and  
Industrial Research, University Buildings, Delhi
25. BHATTACHARYA, D R, M Sc, Ph.D., Dr ès Sciences (Paris), Professor of Zoology  
Allahabad University, 7 Malaviya Road, Allahabad.
26. BOMFORD, LT -COL G, R.E., Survey of India, Temporary Secretariat, Delhi (1935)

- 27 BOSE, N L, M A., D Sc, F L S, Forest Botanist, Forest Research Institute, Dehra Dun (1941)
28. BOSE, D M, M A, B Sc, Ph.D, Director, Bose Institute, 93 Upper Circular Road, Calcutta
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- 30 BOSE, N K, M Sc, Ph D, Mathematical Officer, Punjab Irrigation Research Institute, Lahore (1938)
- 31 BOSE, R C, M A, Lecturer in Statistics, Calcutta University, Presidency College, Calcutta (1912)
- 32 BOSE, S N, M Sc, Professor of Physics and Head of the Department, Dacca University, Ramna, Dacca
- 33 BOSE, S R, M A, Ph D, F R S E, Professor of Botany, Carmichael Medical College, Calcutta (1935)
- 34 BRAHMACHARI, SIR U N, Kt, Rai Bahadur, M A, M D, Ph D, F R A S B, K I H, Physician, Medical College Hospitals, Calcutta (Retired), 19, Loudon Street, Calcutta
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- 38 CHAKRAVARTI, S N, D Sc, D Phil, F C S, F I C, Chemical Examiner to the Governments of U P and C P, 45 Taj Road, Agra (1935)
- 39 CHATTERJEE, N C D Sc, Assistant Entomologist, Forest Research Institute Dehra Dun
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- 41 CHOPRA, B N, D Sc, F L S, Assistant Superintendent, Zoological Survey of India, Kaiser Castle, Benares Cantt (1935)
- 42 CHOPRA, BREVET COL, SIR R N, Kt, C I E, M D, Sc D, F R A S B, F R C P I M S (Retd), Director, Drug Research Laboratory, Jammu-Tawi, Jammu and Kashmir State
- 43 CROWDHURY, J K, M Sc, Dr Phil (Berlin), Reader in Chemistry, Dacca University, Ramna, Dacca (1938)
- 44 CROWDHURY, K AHMAD, B A, B Sc, M S, D Sc, Wood Technologist, Forest Research Institute, New Forest, Dehra Dun (1940)
- 45 COULSON, A L, D Sc, D I C, F G S, Superintending Geologist, Geological Survey of India, Indian Museum, Calcutta (1935)
- 46 CROOKSHANK, H, B S, D Sc, B A I, Capt, A I R O, Superintending Geologist, Geological Survey of India, c/o Garrison Engineer, Razmak (1938)
- 47 DASTUR, R H, M Sc, Cotton Physiologist, Agricultural College, Lyallpur, Punjab
- 48 DATTA, S, M Sc, D Sc, D I C, Principal, Rajshahi College, Rajshahi (1935)
- 49 DATTA, CAPTAIN, S C A, D Sc, F R S E, M R C V S, D T V M, R I A S C, Military Veterinary Laboratory, Lahore Cantt (1938)
- 50 DE, M N, M B (Cal), M R C P (Lond), Professor of Medicine, Medical College and First Physician, Medical College Hospital, Calcutta (1942)
- 51 DESAI, R D, M Sc, D Sc (Lond), D I C, Deputy-Head, Applied Chemistry Department, V J T Institute, Matunga, Bombay (1942)
- 52 DEY, B B, D Sc, F I C, I E S, Professor of Chemistry, Presidency College, Madras
- 53 DHAR, N R, D Sc, F I C, I E S, Deputy Director of Public Instruction, U P, Allahabad
- 54 DHAR, S C, M Sc, D Sc (Cal, Edin), F R S E, Professor and Head of the Department of Mathematics, Nagpur University, Nagpur (1938)
- 55 DIKSHIT B B, Ph D (Edin), M R C P (Edin), D P H (Calcutta), M.B.B.S. (Bombay), Officer in charge, Pharmacology Department, Haffkine Institute, Bombay (1941)

- 56 DUNN, J. A., D Sc, D I C, F G S, Superintending Geologist, Geological Survey of India, Indian Museum, Calcutta (1935)
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- 61 FOWLER, GILBERT J., D Sc, F I C, Consulting Chemist, Central Hotel, Bangalore
- 62 FOX, C. S., D Sc, M I Min E, F G S, F R A S B, Director, Geological Survey of India, Indian Museum, Calcutta
- 63 GEE, E. R., M A, F G S, Geologist, Geological Survey of India, Indian Museum, Calcutta (1935)
- 64 GHOSH, S. L., M Sc, Ph D, Professor of Botany, Government College, Lahore
- 65 GHOSH, B. N., D Sc (Lond), Lecturer in Chemistry, Calcutta University, 92 Upper Circular Road, Calcutta (1942)
- 66 GHOSH, J., M A, Ph D, Professor of Mathematics, Presidency College, Calcutta (1936)
- 67 GHOSH, J. C., D Sc, Director, Indian Institute of Science, Malleswaram, Bangalore
- 68 GHOSH, P. K., M Sc, D I C, D Sc (Lond), Geologist Geological Survey of India, Calcutta (1941)
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- 70 GHOSH, R. N., D Sc, Reader in Physics, Allahabad University, Allahabad (1939)
- 71 GHURRY, G. S., M A, Ph D, Professor of Sociology, University of Bombay, Fuller Road, Bombay (1941)
- 72 GLENNIE, COL. E. A., D S O, R E, Survey of India, Dehra Dun
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- 75 GUHA, B. S., M A, Ph D, F R A S B, Assistant Superintendent, Zoological Survey of India, Kaiser Castle, Benares Cantt
- 76 GUHA, P. C., D Sc, Acting Professor of Organic Chemistry, Indian Institute of Science, Malleswaram, Bangalore (1935)
- 77 HADDOW, J. R., O B E, B Sc, M R C V S, D V S M, I V S, Deputy Director and Officer in-charge, Pathology and Bacteriology, Imperial Veterinary Research Institute, Muktesar-Kumman, U P
- 78 HENDRY, D., M C, B Sc, N D A, Director, Imperial Chemical Industries, India, Calcutta (1938)
- 79 HEBON, A. M., D Sc, F G S, F R G S, F R S E, F R A S B, Mines and Geology Office, Hyderabad (Deccan)
- 80 HORA, S. L., Rai Bahadur, D Sc, F R S E, F L S, F Z S, F R A S B, Director of Fisheries Bengal, 1 Deodar Street, Calcutta
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- 82 ISHAQ, MOHAMMED, M Sc, Ph D, Head of the Department of Physics, Muslim University, Aligarh (1940)
- 83 IYENGAR, M. O. P., M A, Ph D, F L S, University Professor of Botany, Madras University, Triplicane, Madras
- 84 JOSHI, A. C., D Sc, Assistant Professor of Botany, Benares Hindu University, Benares. (1938)
- 85 KAPUR, S. N., Ph D, Officer on Special Duty, Timber Directorate, Department of Supply, New Delhi
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- 87 KOTHARI, D S, M Sc, Ph D, Reader and Head of the Department of Physics, Delhi University, Delhi (1936)
- 88 KRISHNA, S, C I E, Ph D, D Sc, F I C, Forest Biochemist, Forest Research Institute, New Forest, Dehra Dun (U P)
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- 91 KRISHNAN, M S, A R C S, Ph D, D I C, Geologist, Geological Survey of India, Indian Museum, Calcutta (1935)
- 92 LAL, R B M B B S, D P H., D T M & H D B, Professor of Vital Statistics and Epidemiology All India Institute of Hygiene and Public Health, Calcutta (1935)
- 93 LAW, S C M A B L, Ph D, F Z S, M B O U 50 Kailas Bose Street Calcutta (1936)
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- 104 MILLS, J P, M A, I C S, Secretary to H E the Governor of Assam, Government House Shillong Assam (1936)
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- 113 NARLIKAR, V V B Sc (Bom), B A (Cantab), F R A S, Professor of Mathematics and Head of the Department, Benares Hindu University, Benares (1939)
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117. OLVER, COL. SIR ARTHUR, C B., C M G., F R C V S., Principal, Royal Veterinary College, Edinburgh
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120. PARANJPE, SIR R P., Kt., D Sc., Purushottam Ashram, Poona 4
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123. PERCIVAL, F G., O B E., Ph D., F G S., Superintendent of Mines and Quarries Tata Iron & Steel Co., Ltd., 3 Beldih Lake Road, Jamshedpur (1936)
124. PHILPOT, H P., B Sc. (Eng.), M Inst C E., M I M e c h E., M I A E., M I M., Principal and Jodhpur Hardinge Professor of Technology, Engineering College, Benares Hindu University, Benares
125. PICHAMUTHU, C S., B Sc., Ph D. (Glasgow), Registrar, Mysore University, Mysore (1942)
126. PINFOLD, E S. M A F G S., Geologist The Attock Oil Co., Ltd., Rawalpindi
127. PRASAD, B N. M Sc., D Sc. Ph D., Mathematics Department, Allahabad University, Allahabad (1936)
128. PRASAD, MATA, D Sc., F I C. Professor of Inorganic and Physical Chemistry, Royal Institute of Science, Bombay (1935)
129. PRASHAD BAINI, O B E., D Sc., F R S E., F L S., F Z S. F R A S B., Director, Zoological Survey of India Kassar Castle Benares Cantt
130. PRUTHI, H S., M Sc., Ph D. Imperial Entomologist, Imperial Agricultural Research Institute New Delhi
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133. RAMANATHAN K R. M A. D Sc., Superintending Meteorologist, Meteorological Office, Poona 5
134. RAMDAS, L. A., M A., Ph D., Agricultural Meteorologist, Meteorological Office, Poona 5 (1935)
135. RAMIAH, K., M B E., L. Ag., M Sc. (Cantab.), Dip Agr. (Cantab.), Geneticist Institute of Plant Industry, Indore (1942)
136. RANGASWAMI AYYANGAR, G N., Rao Bahadur, B A., I A S. (Retd.), 'Anjali', 10/131 Thiruvengadaswami Road, R S Puram, Coimbatore
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140. RAO, K. RANGADHAMA, D Sc. (Madras and London), Reader in Physics, Andhra University, Guntur (1937)
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142. RAY, B B., D Sc., Khairia Professor of Physics, Calcutta University, 92 Upper Circular Road, Calcutta (1935)
143. RAY, J N., D Sc., Ph D., F I C., Office of the Director-General, Indian Medical Service, New Delhi (1935)
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- 153 SEN, H K, M A, D Sc, D I C, Director, Indian Lac Research Institute, Namkum, Ranchi
- 154 SEN, J M, B Sc, M Ed (Leeds), Dip Ed (Oxford), T D (London), F R G S, Principal Krishnagar College, Krishnagar (1935)
- 155 SEN, N R, D Sc, Ph D, Ghose Professor of Applied Mathematics, Calcutta University 92 Upper Circular Road, Calcutta
- 156 SENGUPTA, N N, Ph D, Professor of Psychology, Lucknow University, Lucknow
- 157 SEYMOUR SKWILL, LT COL R B, C I E, M A, Sc D, F R S, M R C S, L R C P, F Z S, F L S, Zoological Laboratory, Cambridge University Cambridge (1936)
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- 160 SHARIF, M, D Sc, Ph D, Entomologist, Haffkine Institute, Parol, Bombay (1939)
- 161 SHORTT, LT COL H E, C I E, M D, Ch B, D T M & H, D Sc, I M S, Inspector-General of Civil Hospitals, Assam Shillong (1936)
- 162 SIDDIQI, M R, M A, Ph D, Professor of Mathematics, Osmania University, Hyderabad (Deccan) (1937)
- 163 SINGH, B K, M A, Sc D, F I C, I E S, Professor of Chemistry, Allahabad University, Allahabad
- 164 SINGH, B N, M Sc, D Sc, Irwin Professor of Agriculture, University Professor of Plant Physiology and Head of the Institute of Agricultural Research, Benares Hindu University (1941)
- 165 SINTON, LT-COL J A, V C, O B E, M D, D Sc, D P H, D T M, I M S, Malaria Laboratory, Horton Hospital, Epsom, Surrey, England
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- 167 SIRKAR, S C, D Sc, Research Assistant to Palit Professor of Physics and Honorary Lecturer, Calcutta University 92 Upper Circular Road, Calcutta (1942).
- ✓ 168 SONONI, V V, M Sc, Superintending Meteorologist, India Meteorological Department, New Delhi (1942)
- 169 SOKHEY, LT-COL S S, M A, M D, D T M & H, I M S, Director, Haffkine Institute, Parol, Bombay
- 170 SONDHI, V P, M B E, M Sc, F G S, Geologist, Geological Survey of India, Calcutta (1941)
- 171 SOPARKAR, M B, M D, B Hy, 117 Khar, Bombay 21. (1937)
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- 174 SUBRAHMANYAN, V, D Sc, F I C, Professor of Biochemistry, Indian Institute of Science, Bangalore
- 175 SUR, N K, D Sc, Meteorologist, Alipore Observatory, Calcutta. (1938)

- 176 TAWDE, N R, M Sc, Ph.D (Lond ), Lecturer in Physics, Royal Institute of Science, Bombay (1942)
177. TAYLOR, MAJOR-GENERAL, SIR JOHN, Kt, C I E, D S O, M D, D P H, I M S, Director, Central Research Institute, Kasauli (Simla Hills)
- 178 TEMPLE, F C, (Hony Col) A F (I), C I E V D A D C, 28 Victoria Street, London, S W 1 (1937)
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- 180 VACHELL, E T, M A (Cantab ), F G S, F Inst P, Senior Geologist (India), Burmah Oil Company, Digboi, Assam (1942)
- 181 VENKATARAMAN, K, M S Tech, Ph D, D Sc Director, Bombay University Laboratories of Chemical Technology and Textile Chemistry, Bombay (1939)
- 182 VENKATARAMAN, SIR T S, Kt, Diwan Bahadur, B A I A S, Imperial Sugarcane Specialist (Retd ), Ponnurangam Street, R S Puram, Coimbatore
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- 190 YAJNIK, N A, M A, D Sc, A I C, Professor of Chemistry, Panjab University, Lahore (1940)

## HONORARY FELLOWS

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- 2 BAILEY, E B, F R S, Director General, Geological Survey of Great Britain, Exhibition Road, South Kensington, London, S W 7
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- 4 BOWER, F O, Sc D (Cantab ), LL D, F R S, Emeritus Professor of Botany, Glasgow University, 2 The Crescent, Ripon, Yorks
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- 9 EDMUNDS, CHARLES W, A B, M D, Professor of Pharmacology and Therapeutics, University of Michigan Medical School, Ann Arbor, Michigan, U S A
- 10 EINSTEIN, ALBERT, N L, Princeton University, New Jersey, U S A
11. FISHER, R A, Sc D, F R S, Galton Professor in the University of London
12. GOODRICH, E S, M A, D.Sc, F R S, Linacre Professor of Zoology and Comparative Anatomy, University Museum, Oxford
- 13 GREENWOOD, MAJOR M, D Sc, F R C P, F R S Professor of Epidemiology and Vital Statistics, London School of Tropical Medicine and Hygiene
14. HOLLAND, SIR THOMAS H, K C S.I, K C I E, D Sc, F R S, Principal of the University of Edinburgh

- 15 HOPKINS, SIR FREDERICK GOWLAND, Kt, M.A., D.Sc., N.L., F.R.S., Sir William Dunn Professor of Biochemistry in the University of Cambridge
- 16 KEITH, SIR ARTHUR B., M.D., F.R.C.S., LL.D., F.R.S., Buckston Browne Farm, Downe, Farnborough, Kent, England
- 17 LAWRENCE, E. O., Radiation Laboratory, California University, Berkeley, U.S.A.
- 18 MARSHALL, SIR GUY A. K., C.M.G., F.R.S., Director, Imperial Institute of Entomology, London
- 19 ROBINSON, SIR ROBERT, D.Sc., F.R.S., Waynflete Professor of Organic Chemistry in the Dyson Perrins Laboratory, Oxford University
- 20 RUSSELL, SIR E. JOHN, D.Sc., F.R.S., Director, Rothamsted Agricultural Experimental Station, Harpenden, Herts, England
- 21 SHERRINGTON, SIR CHARLES S., O.M., G.B.E., N.L., F.R.S., Formerly Waynflete Professor of Physiology in the University of Oxford, Broomside, Valley Road, Ipswich, England
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## APPENDIX II

### ABSTRACT PROCEEDINGS OF THE COUNCIL, 1942

[Note—These abstracts of the proceedings of the Council relate to questions dealt with which are likely to be of interest to Fellows. Routine matters and matters which are under consideration are not included.]

1 It was resolved to modify the existing regulations regarding preparation of papers for the *Transactions* and *Proceedings* of the National Institute as follows:—

- (i) Date of publication should be printed directly after the author's name
- (ii) The word 'Vol' should be omitted
- (iii) The Vol No. in arabic numerals should be printed in bold type
- (iv) The word 'pp' should be omitted (5-3-42)

2 The General Editor placed before the Council a statement showing the payment made to different Associate Editors for collecting abstracts of their sections and the matter printed off. He suggested that it would be better to base the payment on the matter actually received instead of the lump sum paid per subject.

It was resolved, after discussion, to sanction payment at the rate of Rs 3 per printed page per section. If in any section the matter printed exceeds 50 pages, the question of additional remuneration was to be referred to the Council for decision. (15-4-42)

3 After considering the circular letter from the Government of India, Department of Commerce, regarding economy in the use of paper, it was resolved—

- (i) that it was not desirable to discontinue the Institute's *Proceedings* and *Transactions*,
- (ii) to complete the volumes of *Indian Science Abstracts* for 1938 and 1939 only,
- (iii) to defer printing of the abstracts for 1940 onwards until after the war, the typewritten copy being kept ready for reference in the National Institute's office, and
- (iv) to inform the Government of India of the steps taken to economize in the consumption of paper (5-10-42)

## APPENDIX III

## COMMITTEES, 1943.

## SECTIONAL COMMITTEES

## (1) 'Mathematics' Committee for Mathematics, Astronomy and Geodesy —

	To serve until Dec 31
Dr S K Banerji (Secretary and Convener)	1943
Prof V V Narlikar	1943
Principal B M. Sen	1944
Prof P C Mahalanobis	1944
Prof O V Hanumantha Rao	1945
Prof N R Sen	1945

## (2) 'Physics' Committee for Physics and Meteorology —

Prof P K Kishlu	1943
Prof B B Ray	1943
Dr N K Sur	1944
Dr D S Kothari	1944
Prof S K Mitra (Secretary and Convener)	1945
Dr K R Ramanathan	1945

## (3) 'Chemistry' Committee for Pure and Applied Chemistry —

Dr K Venkataraman	1943
Prof M Qureshi	1943
Dr J K Basu	1944
Prof B C Guha	1944
Prof J N Mukherjee (Secretary and Convener)	1945
Prof K G Nark	1945

## (4) 'Engineering Sciences' Committee for Engineering, Metallurgy, Electro-technics and kindred subjects —

Dr F G Percival (Secretary and Convener)	1943
Mr W C Ash	1943
Dr Gilbert Fowler	1944
Mr D Hendry	1944
Principal H P Philpot	1945
Dr N K Bose	1945

## (5) 'Geology' Committee for Geology, Palaeontology, Mineralogy and Geography

Mr D N Wadia	1943
Mr E S. Pinfold	1943
Dr M S. Krishnan	1944
Mr J. B. Auden (Secretary and Convener)	1944
Mr B Rama Rao	1945
Mr V P Sondhi	1945

## (6) 'Botany' Committee for Pure and Applied Botany, Forestry and Agronomy —

Principal P Parija (Secretary and Convener)	1943.
Prof. S R Bose	1943
Prof. S. P Agharkar	1944
Rao Bahadur G N Rangaswami Ayyangar	1944.
Prof S L Ajrekar	1945.
Dr A C Joshi	1945.

## (7) 'Zoology' Committee for Pure and Applied Zoology and Anthropology including Ethnology.—

	To serve until Dec 31
Dr B S Guha	1943.
Dr H S Pruthi	1943
Khan Bahadur M Afzal Husain	1944
Prof R Gopala Aiyar	1944
Prof G S Ghurye	1945
Dr S L Hora (Secretary and Convener)	1945

## (8) 'Physiology' Committee for Animal Physiology, Pathology, Bacteriology, Psychology and other Medical and Veterinary subjects —

Sir U N Brahmachari	1943
Major General J Taylor	1943
Dr K N Bagchi	1943
Mr F Ware	1944
Lt Col S S Sokhey	1944
Prof N N Sen Gupta	1944
Dr B B Dikshit	1945
Dr K V Krishnan	1945
Dr A C Ukil (Secretary and Convener)	1945.

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# APPENDIX IV.

## THE NATIONAL INSTITUTE OF SCIENCES OF INDIA.

*Receipts and Payments Account for the year ended 30th November, 1942*

### RECEIPTS.

	Rs	As	P	Rs	As	P
To Balance brought forward	51,333	6	7			
" Members' Admission Fees	160	0	0			
" Subscriptions	6,159	13	0			
" " Subscriptions in advance	18	6	0			
" Contributions towards publication of 'Indian Science Abstracts'	50	0	0			
" Sale of Authors' extra copies and publications	256	0	0			
" Interest on Investments	1,627	11	0			
" Grants-in-aid—						
Government of India	6,000	0	0			
Universities	1,000	0	0			
Grants towards publication of Papers	7,000	0	0			
" Miscellaneous Receipts	500	0	0			
	5	4	0			

	Rs	As	P	Rs	As	P
By Salaries of Staff	2,471	10	9			
" Printing Circulars, Notices, etc	99	12	0			
" " Publications, Reports, etc	6,648	13	6			
" Contributions to other Science Academies under Rule 19	1,104	0	0			
" Honoraria, etc for preparing Abstracts for 'Indian Science Abstracts'	250	0	0			
" Postage	393	3	3			
" Stationery	85	6	9			
" Audit Fee	50	0	0			
" Travelling	250	0	0			
" Rent of Office	600	0	0			
" A R P Expenses	74	14	6			
" Miscellaneous Expenses	114	7	0			
" Bank Charges	39	10	0			
" Cash and Other Balances—						

Investments—			
3½% G P Notes 1842/43	5,000		
3½% " 1854/55	2,000		
3½% " 1865	6,000		
3½% " 1879	2,000		
3½% " 1900/01	8,000		
4% Loan 1960/70	17,000		
	40,000		

At cost 40,786 13 10

With Imperial Bank of India—

	Rs	As	P
On Savings Bank Account	5,757	4	0
On Current Account	8,383	8	6
	14,140	12	6
In hand	1	0	6
	54,928	10	10

TOTAL 67,110 8 7

TOTAL 67,110 8 7

Examined with the Books and Vouchers and found in accordance therewith  
PRICE, WATERHOUSE, PEAT & CO } Auditors  
Chartered Accountants,  
Registered Accountants

CALCUTTA,  
9th December, 1942



## APPENDIX VI.

## BUDGET ESTIMATES

	1941-42 Estimates	1941-42 Actuals	1942-43 Estimates
<i>Ordinary Receipts</i>			
Subscriptions	Rs 5,500	Rs 6,178	Rs 6,400
Interest	1,500	1,028	1,650
Contributions towards publication of 'Indian Science Abstracts'	100	50	50
Sale of publications including 'Indian Science Abstracts'	500	256	200
Grants-in aid from Universities	1,000	1,000	1,000
Grants-in aid from Government of India	7,000	6,000	6,000
Grants towards publication of papers		500	
Miscellaneous Receipts		5	
Contributions from Opening Balance	3,800		2,725
	<u>19,400</u>	<u>15,617</u>	<u>18,025</u>
<i>Extraordinary Receipts</i>			
Admission Fees	320	160	416
<i>Ordinary Payments</i>			
Salaries and Allowances	9,300	2,472	2,000
Publications other than 'Indian Science Abstracts' and Circulars	12,000	6,749	7,000
*Publication of 'Indian Science Abstracts'			5,000†
Honoraria, etc for preparing abstracts for 'Indian Science Abstracts'	1,000	250	1,000
Contributions to co-operating Academies under Rule 19	1,200	1,104	1,200
Postage	600	393	600
Stationery	150	85	100
Audit Fee	50	50	50
Travelling	400	250	250
Office Rent	600	600	600
A R P Expenses		75	75
Miscellaneous Expenses (including Bank charges)	100	154	150
Balance credited to General Fund		3,435	
	<u>19,400</u>	<u>15,617</u>	<u>18,025</u>
<i>Extraordinary Payments</i>			
Funding of Admission Fees	320	160	416

\* Additional provision has been made to cover the increased cost of paper and publications

† This sum is set apart for completing 'Indian Science Abstracts' for 1938 and 1939



# Annual Address to the National Institute of Sciences of India.

CALCUTTA, 1943

*By DR B PRASHAD, OBE, DSc, FRSE, FLS, FRASB*

## CONSERVATION OF WILD LIFE IN INDIA

### I GENERAL

I regret to have to start my short address this year with an apology to the Fellows of the Institute for not being able to devote sufficient time to the activities of the Institute, but this was rendered impossible by circumstances over which I had no control. The headquarters of my Department were suddenly shifted from Calcutta to Benares, and owing, firstly, to my being so far away from the headquarters of the Institute at Calcutta, and, secondly, the pressure of official duties I could spare very little time for the work of the Institute. In fact, foreseeing that something like this was likely to happen, I had great hesitation in agreeing to carry on as the President of the Institute during 1942, but my colleagues on the Council did not agree with my views and I was left with no choice except to fall in with their wishes. Under the circumstances, I am afraid, I have been the President of the Institute in name only, at least during the greater part of the year.

Since the last meeting at Baroda the affairs of the Institute have been progressing more or less satisfactorily, and notwithstanding the great stress due to the world war, the unfortunate disturbances in the country, as also the consequent economic conditions, there has been no great change in our material prosperity during this period. The annual grant from the Government of India, as is explained later on, was reduced to its 1940 figure and we have not received any fresh donations during the year, but it is to be hoped that these are only temporary setbacks and that the Institute will, with the return of normal conditions, begin to receive more active support both from the Central and Provincial Governments, the Universities and the well-wishers of science all over the country. The record of our activities during the past year, as detailed in the Annual Report, is a matter of satisfaction and reflects great credit on the administrative officers and the Council for the very careful way in which the affairs of the Institute have been handled during these critical times.

The number of Fellows on our roll at the beginning of the year was 179  
**Fellows.** Ordinary Fellows and 23 Honorary Fellows. At the end of the year this number stood at 177 Ordinary Fellows and 22 Honorary Fellows. During the year one Ordinary Fellow resigned, and the

Institute lost one Honorary and one Ordinary Fellow by death. As was stated in my address last year, the number of Fellows of the Institute, considering the prevailing conditions of the country and the statutory limitations in regard to new elections, is satisfactory. The change in the rules, which was adopted in the Benares meeting of 1941, has made it possible to increase the annual number of Fellows to be elected from 10 to a number not exceeding 15, dependent on the vacancies occurring during the previous year by resignation, death, or otherwise, until the maximum of 250 is reached. As a result of this change thirteen Ordinary Fellows were elected in 1942.

Owing to the unfortunate situation prevailing in the country only one General Meeting was held at Calcutta in the rooms of the Royal Asiatic Society of Bengal on the 5th of October, 1942. Another meeting was proposed to be held in Benares, but for various reasons the arrangements for the meeting could not be completed, and the Council was obliged by the prevailing conditions to give up the idea of holding the proposed meeting at Benares or at any other centre in the country. It is hoped that during the present year conditions will change materially, and it would be possible to arrange for more meetings of the Institute at various centres.

The Council for 1942 was elected at the Seventh Annual General Meeting held at Baroda on the 1st January, 1942, and with only one change, served throughout the year. The change was due to the resignation of Dr B S Guha, our Honorary Treasurer, who resigned owing to the transfer of his office from Calcutta, and I am grateful to Prof J N Mukherjee, one of our Vice-Presidents, for so kindly agreeing to take over the arduous duties of the Honorary Treasurer. The Council held five meetings during the year. At its meeting of the 5th October, 1942, it was resolved to appoint a Committee consisting of the two Honorary Secretaries, the Honorary Treasurer and Rai Bahadur Dr S L Hora, Editor of Publications, to act on behalf of the Council in consultation with the President, the decisions of the Committee were to be reported subsequently by post to the members of the Council for information. This course was rendered necessary, as owing to the abnormal conditions prevailing in the country it was found difficult to have the necessary quorum at the meetings of the Council. The proposal was approved at the Ordinary General Meeting held on the 5th October, 1942, and the Committee has been carrying on the work of the Institute very satisfactorily. I have to express my grateful thanks to the very efficient way in which the members of the Committee have carried on the work of the Institute since this date.

Three numbers of the *Proceedings* and two numbers of the *Transactions* have been published during the year. Considering the very unsettled conditions in the country and the difficulties for obtaining the necessary amount of paper for our publications this record is very satisfactory. The Fellows of the Institute, I am sure, realize the heavy

work involved in the editing of our publications and seeing them through the press, and join with me in expressing our gratitude to Rai Bahadur Dr S L Hora, the Editor of our publications, for his work in this connection. We are also grateful to our printers, Messrs Baptist Mission Press of Calcutta, for the expeditious printing of our publications. Printing of publications, owing to the great scarcity of paper in the country, is likely to be a difficult matter hereafter, but it is hoped that it will be possible to continue to issue our publications even though at a reduced rate. If it is at all necessary, the Council should approach Government for giving the Institute special priority for obtaining necessary quantities of paper for its publications.

The Government of India unfortunately found it impossible to sanction the increased grant of Rs 7,000 for the current financial year, and this, owing to the great increase in the prices of paper and printing, has meant a great strain on the meagre funds of the Institute. It would be a very serious matter indeed if for want of funds or any other reasons the Institute is obliged to stop or curtail its publications beyond a certain limit. It is, therefore, hoped that the Government will kindly reconsider the position next year and give us an increased grant to make it possible for us to continue our publications and thereby provide a medium of publication for the daily increasing output of scientific research in the country.

In my address, last year, I directed attention to the impossibility of the work of the publications of a learned society like ours being carried on by any one editor without the active help and support of a number of workers all over the country. I also remarked that for a work like the *Indian Science Abstracts* it is essential to have a permanent staff for the timely preparation and publication of the Abstracts. Unfortunately, the prevailing conditions in the country did not make it possible for the Council to appoint any additional staff, and further, our Assistant Secretary, Mr C O Bateman, who had been so efficiently looking after our publications, was also not available owing to ill-health during the major part of the year. This has been responsible for a certain amount of delay in our publications.

During the year under review, the Government of India in a circular letter on the subject of economy of paper, suggested that Associations may discontinue certain periodical publications during the war and revise their publication programme. The Council of the Institute, after careful consideration of this proposal, decided to suspend publication of the *Indian Science Abstracts*, after completing the volumes for 1938 and 1939 which are in the press, until after the war. The preparation and compilation of the *Indian Science Abstracts* for the subsequent years, however, will be continued and the typescript kept in the office of the Institute for reference by Fellows.

The preparation of a Quinquennial Review dealing with the progress of science in the country could not also for the same reasons be taken up during 1942. I am afraid, this undertaking will have to be postponed till more propitious times.

The financial position of the Institute is detailed in the Balance Sheet appended to the Annual Report. Our expenses, as will be

**Finances** seen from the Balance Sheet, are definitely on the high side, more particularly in connection with our publications. This, as I remarked last year, is a very serious matter, more particularly as the cost of publication is increasing from day to day, and the Institute has, as already noted, not only not received any fresh grants-in-aid, but the increased annual grant which was sanctioned by the Government of India last year, has also been reduced to its previous figure of Rs 6,000. In addition to the Government of India grant the Institute received the following grants during the year —

- (1) Rs 500 from the Calcutta University
- (2) Rs 300 from the Osmania University
- (3) Rs 200 from the Dacca University

These annual grants are hardly enough even for maintaining the ordinary activities of the Institute, and the Council will soon have to approach the Provincial Governments, and other Universities in the country for sanctioning grants-in-aid if the Institute is to carry on its work satisfactorily. As a measure of economy the Council have decided to dispense with the services of our Assistant Secretary, Mr C O Bateman, from the beginning of 1943, and not to fill up the post for the duration of the war. This will mean a great deal of extra work for our executive officers, but the Council faced with a material reduction in our income and the increased expenses has rightly taken this step.

There is very little to comment upon in the way of development of scientific research in the country to what I stated in my address last year, but attention may be directed to the fact that in view of the urgent war requirements a great deal of attention has been paid during the year to applied scientific and industrial research. Scientific research in basic sciences has generally been relegated to the background while the prevailing conditions in the country during the year made it impossible for workers and teachers being able to devote sufficient time or attention either to research or the teaching of science. Special mention may here be made of a further development in the constitution of the Board of Scientific and Industrial Research and the Industrial Utilization Committee which were established by the Government of India in 1940 for co-ordinating and generally exercising administrative control over the ever-expanding activities of these two organizations. The Government of India have recently constituted a Governing Body of the following (1) the Hon'ble Member of the Council of His Excellency the Governor-General in charge of the portfolio of Commerce (*Ex-officio*), (2) a representative of the Commerce Department of the Government of India, appointed by the Government of India, (3) a representative of the Finance Department of the Government of India, appointed by the Government of India, (4) two members of the Board of Scientific and Industrial Research

elected by the said Board, (5) two members of the Industrial Research Utilization Committee elected by the said Committee, (6) the Director of Scientific and Industrial Research, and (7) one or more members to be nominated by the Government of India to represent interests not otherwise represented. The functions of the Board have been further elucidated, and it has also been decided that a fund, viz., the Industrial Research Fund, should be constituted by grants from the Central Revenues to which additions will be made from time to time as funds become available from other sources. These 'other sources' will comprise grants, if any, by Provincial Governments, by industrialists for special or general purposes, contributions from Universities or local bodies, donations or benefactions, royalties, etc., received from the development of the results of industrial research, and miscellaneous receipts. The Council of Scientific and Industrial Research will exercise full powers in regard to the expenditure to be met out of the Industrial Research Fund subject to its observing the bye-laws which will be framed by the Governing Body of the Council, from time to time, with the approval of the Governor General-in-Council. For extending the work of the Board, it has been suggested that Provincial Advisory Boards of Scientific and Industrial Research should be established by the Provincial Governments to form liaison with the Central Board. Welcome as these developments are, it is unfortunate that more representatives of principal scientific bodies, societies and Universities from different parts of the country have not been included either in the main Board or the Council of Scientific and Industrial Research. Our Institute has been pressing for such representation since the date when the establishment of these bodies was first contemplated, and it is hoped that authorities concerned will take steps to make good this omission at an early date. Mention may also be made of the establishment of a Utilization Branch of the Geological Survey of India, this should ensure the rapid development of the mineral resources of the country, and add fresh laurels to the brilliant achievements of the oldest scientific service in the country.

It would be a truism to reiterate that we are living in times when great

confusion of thought pervades almost all spheres of life

**Future.**

As a result of scientific advances and their application to modern warfare most well-established values on which man used to base his sense of security have lost nearly all significance. Naturally under such conditions of stress and turmoil, which are influencing practically all spheres of life, doubts and fears are expressed about all plans and programmes of development, and the suggested remedies often appear contradictory and conflicting. Scientists are equally influenced by this unstable state of affairs, and there can be little doubt that if they are to serve the best interests of humanity—for that after all is the *sine qua non* of all progress, whether scientific or otherwise—they can no longer continue to develop as pure *Scarabees*. In addition to being specialists in some scientific subject they must, one and all, have a good knowledge of various social sciences, and

become as conversant as possible with the pressing needs and problems of humanity as a whole. Equally with this training of the scientists more attention will have to be paid to the education of the general public in matters pertaining to science and its applications. These two essentials are, both of them, undoubtedly long-term projects, but if scientists are to do more than simply act in an advisory capacity dealing with special problems as they arise and without reference to their social contacts, it is undoubted that these two essentials must receive urgent consideration at the hands of the Government and the scientists themselves. Carefully considered long-term programmes must be drawn up in regard to the future of science and scientists, and in this connection it is urgent that the importance of organizing scientific effort should be fully realized. It is also essential to emphasize that the development of pure science should not be curtailed as a result of such organization, for as Professor Bernal so eloquently expressed in a recent article 'There is no reason, however, for the fear that as a result of the experience of the war the development of free science will be curtailed or stunted. Effective organization of science implies neither an exclusive concern with problems of immediate application nor the subjecting of scientists to the discipline of a rigid and unimaginative bureaucracy. Those who have been working for an improvement of the present chaotic system of science in the direction of using it more effectively for human welfare realize fully that any such development would immediately frustrate their ends. If applied science was exclusively followed, the basic principles on which any new development, however practical, must depend would never be elucidated.'

Unfortunately, almost all developments in India within recent years have been directed towards the organization of Applied Science as opposed to Pure Science. The importance of this development cannot be underrated but more attention must be paid to see that with the development of Applied Science more facilities are provided for pure scientific studies and research, and it is in this connection that the National Institute of Sciences can render invaluable service to the country. Pure Science also requires not only increased endowments but more equipment, for as Professor Armstrong has rightly summed up 'Good workshops and good teachers mean able students and first class research—a steady flow to a progressive industry.' Let us hope that this point of view will not be lost sight of by the authorities in this country and that as soon as conditions permit, efforts will be made by our Institute to have better facilities provided for the development of Pure Science equally with those provided for applied scientific work.

## II CONSERVATION OF WILD LIFE IN INDIA

Compared with other living creatures man is relatively a new-comer on the face of the earth. Even according to most liberal estimates primitive man did not appear till about a million years ago. In this relatively short

period he has developed from a very primitive creature to a highly evolved dominant personality on the face of the earth. Man in the course of this period passed through various stages of development which, according to the material used by him for his tools, are respectively named the Stone Age, the Bronze Age and the Iron Age. In very early stages he began by shaping tools from bits of stone or bone, and it was only later that through gradual and hard experience he learnt to work metals which have played such an important rôle in the evolution and development of the present-day civilization. During this period of earth's history man has very materially influenced the plant and animal worlds, and his relationships with both these have become extraordinarily varied and intricate. In the earlier stages man's relations with at least the larger animals were those of direct competition in a very keen struggle for existence. The animals supplied the major part of his food and primitive clothing and various other products that he required for his very simple way of life. Later, however, when he assumed greater mastery over the surroundings in which he lived, he, in addition to agriculture, took to domesticating certain classes of animals for making them his help-mates and companions. Several of them, such as the cattle and the horse, not only proved invaluable in connection with the advance of civilization but gradually made it possible for man to occupy the proud position which he holds on the face of the earth today. *Inter alia* it may be noted that authorities are at variance in regard to the exact sequence of the agricultural and animal husbandry activities of early man. Modern man through horticulture and animal husbandry has developed numerous varieties of cultivated plants and domesticated animals which have made available a very large range of food materials for his use. With the advance of civilization has also been perfected a very complex and rapid system of communication and transportation, and this renders it possible for man to enjoy not only the seasonal products of one area, but of almost all parts of the world. In fact, as a result of these developments animal and plant products from different areas are, in normal times, easily distributed all over the globe.

No substitutes for plant and animal products, which are so essential for human existence, have so far been discovered and in spite of all scientific advances, man is still and will remain dependent on plant and animal worlds for his continued existence. In both international and national interests, therefore, it is of the utmost importance that carefully considered long-range programmes for the conservation of wild life be adopted all over the world.

In earlier times extensive areas of undisturbed forests and uninhabited parts in almost all countries provided safe sanctuaries where wild life was able to survive and even flourish, but changed conditions as a result of the rapid advance of civilization and over-population, the gradual conquest of forests and grass-lands, the opening up of new roads and waterways, and highly improved methods of transport have today left very few areas where wild life can continue to live undisturbed by man. These factors have had and are

continuing to have a very devastating effect on wild life. With these developments fortunately a gradual change is taking place in man's outlook towards Nature. This change is due to the spread of education, and the realization of man's dependence on natural resources. Apart from humanitarian measures, authorities are gradually becoming alive to the inherent dangers underlying the uncontrolled destruction of wild life. This movement for the protection of Nature and so of wild life had its origin barely 50 years back. Though the European nations paid a fair amount of attention to this highly important question, it was the Americans who led the field and set an example as to what could and ought to be done for the preservation of wild life. In the United States of America particularly the occupation and development of vast outlying stretches of the country, the extensive spread of agriculture and consequent disappearance of forests and grass-lands, the drainage of lakes and marshy areas, and the ever-increasing demands of industry have been responsible for a very great reduction in wild life, both of plants and animals. The tragedy was fortunately foreseen fairly early and has been averted, though only to a very limited extent, by the establishment of extensive National Parks or Reserves which, it was hoped, would provide inviolable sanctuaries for and preserve wild life. Such sanctuaries, originally established in the United States of America, have since been set apart in Canada, New Zealand, Australia and the Union of South Africa. In the Kruger National Park, which was founded in 1898 as the Sabi Game Reserve and changed into the Kruger National Park in 1926, South Africa has one of the most extensive and well-managed sanctuaries. Mention may also be made of 'Parc National Albert' in Belgian Congo, which was created by a Royal Decree in 1925 and greatly enlarged in 1929, in 1934 by a Royal Decree its functions were greatly extended and entrusted for management to the Institute for the National Parks of the Belgian Congo which was established with its headquarters at Brussels. This National Park was due to the incessant efforts of the great naturalist, Carl Akeley, an American nature-lover who devoted all his energies to its establishment. In addition to preserving the rapidly dwindling fauna of the area, this park has saved from almost certain extinction the Gorilla, which next to man is the King of Primates. Protection of Nature movement in Germany and adjacent countries proved very valuable in connection with the conservation of wild life in the areas concerned, and extensive National Parks were established in Switzerland, Germany, Italy, Sweden, Spain, Holland and Czechoslovakia. The cause of conservation was further advanced by various International Conferences. In 1900 the British Government convened an International Conference in London for the preservation of animals, birds and fish in Africa. The convention was signed by seven powers interested in Africa, and was to remain in force for 15 years. In 1913 an International Conference for the Protection of Nature was held in Berne at which 17 Governments were represented. The main result of the work of this conference was to establish a central organization for dealing with the question of wild life preservation on an

international basis The world war of 1914-18 unfortunately greatly delayed the adoption of the recommendations of the Berne conference

In 1903 a society for the protection of the fauna of the empire was founded in England by Mr E N Buxton 'with the object of awakening public interest in the assemblages of wild fauna still surviving in every part of the British Empire, and taking such steps as may be possible to save them from extinction, further to co-operate with kindred societies in the Dominions and Colonies or in foreign countries with regard to any conjoint efforts' After the world war of 1914-18 greater attention was directed towards the preservation of fauna in most parts of the world, for as was so well expressed by the president of the society, the Rt Hon Earl of Onslow, 'The whole world is becoming so speedily opened up to travellers, traders, tourists and settlers, and so much uncultivated land is coming under the plough that unless some more or less drastic measures are taken to preserve the distinctive fauna it must obviously disappear entirely' The society started active work for the preservation of the fauna of the empire soon after the world war, and its revised rules, which were passed on April 27, 1928, were brought into force from 1st of May, 1928 Since this date the society began to wield a great deal of influence in connection with the preservation of the fauna of the empire Reference may also be made here to the American Society for International Wild Life Protection and the Dutch Society for the International Wild Life Protection, which have done a great deal to further the cause of conservation of wild life in their respective spheres In 1931 at the instance of the French Government an important International Conference for the Protection of Nature was arranged by the staff of the Natural History Museum of Paris Representatives of Belgium, Czechoslovakia, Germany, Great Britain, Holland, Italy, Latvia, Norway, Poland, Rumania, Spain and the United States of America attended the conference, and very useful spade work was carried out for the formation of a central official international organization for the protection of wild life An International Conference for the protection of the fauna and flora of Africa was convened in London in 1933 As a result of its deliberations it drafted a convention for the better preservation of the fauna of this continent Among the measures suggested were the establishment of sanctuaries, National Parks, Strict National Reserves and other Reserves The conference recommended that all settlements in National Parks should be controlled so as to ensure that as little disturbance as possible is occasioned to the natural fauna and flora It also recommended that special steps should be taken to restrict the export and import of trophies, to stop the use of motor vehicles or aircraft for the purpose of hunting, killing or capturing or driving away, stampeding or disturbing animals, and finally the use of poisons or explosives or poisonous weapons or the use of nets, pits or enclosures, gins, traps or snares, or of set guns and missiles containing explosives for hunting animals should be prohibited Mr E C Stuart Baker, who is a recognized authority on Indian birds and wild life, attended this conference

as one of the observers on behalf of India. In a report, which he submitted to the India Office, he concluded that the results embodied in the report of this conference provided a valuable basis for any measures that may be under consideration for the preservation of indigenous flora and fauna of India. With a view to deciding whether it was desirable for the Government of India to become a contracting party to the convention, either in whole or in part, he suggested that the report should be considered by the Government of India at a special conference of representatives of the Government of India, the Provincial Governments, the Indian States and the adjoining territories of Nepal, Bhutan, etc. About the same time the Society for the Preservation of the Fauna of the Empire in London addressed a letter to the India Office directing attention to the urgent necessity for the protection of wild life in India. With the letter it supplied memoranda dealing with the position of indigenous game in some of the provinces and offered to supply expert advice in case the Government of India decided to arrange for a conference on the subject. Meanwhile the Bombay Natural History Society, which ever since its foundation in 1883, has by intensive propaganda and through the medium of its *Journal* and various publications been rendering very useful service in creating and stimulating interest in the wild life of the country, started publishing in 1934 a series of beautifully illustrated articles on the wild animals of the Indian Empire and the problem of their preservation. This series of articles provided a detailed account of the distribution of mammals in the country together with illustrations of the more important mammals, and the condition of game in different parts of the country including Burma. The articles were written by authorities with intimate first-hand knowledge of the problems of the different areas, and as a result it was possible for the authors to indicate exactly the measures that should be taken for the protection of wild life in the different parts, as also of how these measures could be best given effect to. The Government of India also had been alive to the urgency of the situation and at their instance detailed enquiries in connection with the protection of game were being carried out all over the country. After the preliminary enquiries were completed, the Government of India convened an All-India Conference for the Preservation of Wild Life at Delhi in January 1935 with a view to reviewing the position of the fauna and flora as it existed at the time and considering generally the protection of the animals peculiar to India. The conference adopted a set of resolutions and prepared two lists of species, first of animals that were to be protected as completely as possible, and second of those which 'while not requiring such rigorous protection', shall not be hunted, killed or captured except under license granted by competent authorities. The conference laid special stress on the establishment of wild life sanctuaries, and desired the contracting parties to explore the possibilities of establishing sanctuaries in which hunting, shooting, killing or capturing of all animals was to be prohibited except under the control of the authorities responsible for the management of the sanctuaries. It was agreed

by the conference that the duty of preserving the fauna should be assigned to the forest departments in the areas under their charge, but at the same time urged the necessity of co-operation of police and magistracy in carrying out the necessary measures of protection. Resolutions were also passed for the closest co-operation between the forest departments and Associations that may have been or are established with a view to the preservation of game and wild life. It also laid stress on the introduction of nature study in the country and for carrying out such propaganda as would popularize with the general public the urgent necessity of preserving wild life, as without public support no efforts to preserve wild life would be really effective. It, therefore, recommended that societies for the protection of wild life in the country should make propaganda a principal part of their work. This was further stressed by the chairman of the conference, the late Sir Fazl-i-Hussam, the Hon'ble Member in charge of the Department of Education, Health and Lands of the Government of India, in his closing remarks: 'Even at this stage, I would repeat one point and that is you should not expect much from the Provincial Governments or legislatures, but if you do propaganda in the right direction in the provinces where the power will rest, you will achieve your object.' As a result of the deliberations of this conference an All-India Convention for the preservation of fauna of India was drafted. It was hoped that the convention would be adhered to by all Provincial Governments and the States, and that the signatories of the convention would adopt all possible measures for the protection of the wild life in the areas under their jurisdiction.

Here it would be useful to include a short summary of the legislative measures which were in force for the protection of wild life in British India prior to the date of the All-India Conference for the Preservation of Wild Life. These measures consisted of (1) Wild Birds and Animals Protection Act of 1912, and (2) the Indian Arms Act—both of which were applicable to the whole of British India, (3) the Provincial Game Rules under the Act of 1912, (4) Provincial Forest Act and Rules thereunder, and (5) Provincial Acts dealing with protection. The Provincial Game Rules and Forest Acts had unfortunately been drawn up rather haphazardly and were often contradictory. In addition, no definite authorities had been set apart for enforcing these legislative measures particularly in regard to the poaching and the indiscriminate destruction of game, etc. There was no control of trade in meat, hides, skins and trophies, and at the same time there was no provision for the restriction of the modern methods of traffic such as motor cars and aeroplanes which were proving disastrous to wild life all over the world. Cases of shooting animals from motor cars after they became exhausted as a result of long chase had been reported. A more up-to-date and comprehensive measure was enacted in the Punjab in the Punjab Wild Birds and Wild Animals Protection Act of 1933, while the rules made thereunder provided for the better protection and preservation of certain wild animals including birds and fish. It later resulted in the appointment of a Game

Warden for seeing that the rules were strictly enforced and the protective measures were as comprehensive as far as possible. In addition, under the rules, District Fauna Committees were to be established in all districts for performing functions assigned to them under the rules and for advising generally about the protection of the fauna in their respective districts. Acts on similar lines were also passed in the Central Provinces in 1934 and the United Provinces in 1935, while measures were under consideration in other provinces. Mention may also be made here of the Bengal Rhinoceros Preservation Act of 1932, which prohibited the killing, injuring or capturing of wild rhinoceros in Bengal. Under the Act every wild rhinoceros killed or captured otherwise than by permission was to be the property of the Local Government and stiff penalties were provided against contravention of the Act. A small sanctuary for the preservation of rhinoceros in Bengal was also established in Jalpaiguri district. In 1934 a very great advance was made in the United Provinces through the great personal interest taken by the enlightened Governor of the Province, Sir Malcolm Hailey (now Lord Hailey), as a result of which the National Parks Act of 1934 was passed. This Act provided for the establishment of National Parks and for the preservation of wild animal life or other objects of scientific interest and for incidental matters provided therein. As a result the Hailey Park was demarcated as a National Park in the famous Pathi Doon and the hill forests to the south of it consisting roughly of an area of 99.07 square miles. Under the Act the word 'animal' was defined as 'mammals, reptiles or birds', and it was an offence to kill, injure or disturb any animals or to take or destroy any eggs or nests of any birds in the park. The conditions under which the people were allowed to enter or reside in the park were laid down in the Act and were to be enforced by the forest department. In Assam certain areas had already been demarcated as game sanctuaries and more stringent action was being taken to preserve wild life which according to some reports had been reduced by almost 75% within recent years. Reference may also be made here to the Chamrajanagar Sanctuary of the Mysore State Forests which had been established with a view to offering complete immunity for animals and thereby making it possible for them to thrive without interference. Introduction of other animals not found in the area was to be attempted, and the sanctuary was to provide facilities for the scientific study of the life-histories of different indigenous species of game.

Mention may also be made of the valuable work which the Association for the Preservation of Game in the United Provinces has been carrying on ever since its foundation. After the All-India Conference for the Preservation of Wild Life this Association extended its sphere of work to the whole of India, and in July 1936 started publishing a journal entitled *The Indian Wild Life*. Its aims and objects are very comprehensive, and the two Honorary Secretaries, Major J. Corbett and Mr. Hasan Abid Jafry, have been carrying on valuable work in connection with the protection of wild life throughout British

India and in most of the Native States as well. Unfortunately, owing to the abnormal conditions resulting from the war, the membership of the Association has fallen off and it has had to stop publication of its journal, but it is to be hoped that this is a temporary setback, and before long it will be possible for the Association to restart publication of its journal and carry on its activities on a more extensive scale

From the above it will be seen that a certain amount of spade work had been done and various provinces were becoming alive to the urgency of adopting measures for the protection of wild life in the areas under their control. Unfortunately, however, only one aspect of the conservation of wild life had been considered in all these plans, *viz*, that of the protection of game mainly from the point of view of sport. Further, in all the measures suggested and partially adopted the work, except in the Punjab, was to be carried out by agencies which were already overburdened with work, and naturally the task of looking after wild life was something which it was not possible for them to carry out efficiently in addition to their normal work.

The problem of wild life conservation is not, however, so simple as would appear from the measures which have been taken in this country so far. In fact the multiplicity of the problems involved in any scheme of wild life conservation has begun to be realized only within very recent years. The greatest advances in this connection have again been made in the United States of America, where under the President's Reorganization Plan No. III a Bureau of Biological Survey was constituted on June 30, 1940, by the consolidation of the Bureau of Biological Survey and the Bureau of Fisheries, this Bureau is responsible for the conservation of wild life in the extensive continental area of the United States of America.

It is not possible to give in this address a detailed analysis of all the factors which must be considered in detail in connection with any scheme of wild life conservation, but it is essential to point out that, if wild life conservation is to be a success, the conservation of soil, waterways, forests and grass-lands must receive simultaneous attention. The disastrous effects of man's activities on soil and water resources, whether direct or indirect, conscious or unconscious, are very serious indeed. As an example of direct and conscious influence of man on waterways may be mentioned the pollution of rivers, streams, lakes, etc. through the dumping of huge quantities of refuse and sewage of large cities, as also of the untreated raw wastes of large industrial concerns. Such pollution materially affects plant and animal life of these waters, and has been known in many cases to have destroyed extensive and valuable fisheries. Indirect and unconscious destruction of soil for agricultural developments has similarly done a great deal of harm. In this connection it is unfortunately seldom realized that most schemes of development of large tracts of country, whether as living centres or as agricultural land, unless carefully planned, often have very serious repercussions on the plant and animal life of the area. Nature works in a vicious circle and the interdependence of all these factors is

now fully recognized by all authorities. It would suffice, therefore, to point out that uncontrolled deforestation or the utilization of grass-lands for agriculture and other purposes results in a great erosion of the soil and reduction of rainfall. Rivers, streams and other waterways become silted resulting in the flooding of adjacent areas, and water conservation becomes a very pressing question. With the fall of waterlevel the country in general becomes dry and barren. The land becomes almost useless for agriculture and does not produce even enough of grass or fodder. The repercussions of all these on the wild life in the area are equally serious, as with the disappearance of grass-lands and forests very few sanctuaries are left for wild life.

To undo even a small amount of the damage to organic resources which has resulted from the rapid spread of civilization would require carefully planned long-term programmes of reconstruction, and the development of new social concepts in regard to colonization, agriculture, irrigation, forestry and other allied activities of man. In its broadest sense, conservation of organic resources, as has been so well summed up by I. N. Gabrielson, the Director of the Fish and Wildlife Service of the United States Department of the Interior, 'means restoring to the highest possible level and maintaining in a state of high productivity those resources, including wild life, that can be used on a crop basis to sustain human society'. It will be clear, therefore, that in connection with any scheme for wild life conservation measures must also be adopted for ensuring that soil, water resources, forests and grass-lands are equally conserved.

In wild life management the existence and operation of ecological communities in the domain of nature and man's relationships to them has to be recognized and also the fundamental fact that man's activities often have been and are responsible for disturbing ecological communities. For all schemes of wild life conservation it is essential, therefore, to attempt to restore natural balance which has been and is being disturbed by human activities. With increased occupation of outlying countries resulting in deforestation and disappearance of grass-lands, soil erosion becomes a material menace, rainfall decreases and the problem of water conservation becomes more and more acute. Land gradually becomes impoverished and is not capable of producing enough for the human beings in the area, much less of providing food and shelter for wild life. In all recent schemes of wild life management, therefore, the questions of soil erosion and programmes of re-forestation and increasing grass-land areas are considered as important as the direct measures for the protection and conservation of wild life. With the information at present available most conservation programmes must of necessity be of an experimental nature. They should deal with a few species in restricted areas so that the results could be properly watched and tabulated. Only such work will gradually enable us to acquire the much-needed data and technical knowledge for evolving proper schemes of general ecological management. Meanwhile wild life management must be planned on the ecological and biological

data that are at present available. In the large area of the sub-continent of India the problems of wild life conservation are bound to be very complex, but as soon as possible a programme of conservation must be formulated which would deal not only with the necessity of preserving a few species of game but the conservation of animal and plant life in general.

Recently the Hon'ble Sir Jogendra Singh, Member for Education, Health and Lands of the Government of India, in his address to the meeting of the Board of Forestry rightly stressed the responsibilities of the forest officers in regard to tree plantations in villages. He remarked that

'The need of 7,000,000 villages in the matter of tree plantation has so far received scant attention. It may be useful to take a group of villages and start plantations. Land should be rented for the purpose and trees planted to provide fuel and timber and the grass for feeding the cattle. These village plantations may prove of great economic value, saving the cow-dung for manure, and may even provide large quantities of material for making humus and manure.'

Indicating another direction in which he felt forest officers could do useful work, Sir Jogendra Singh referred to the vast areas which owing to climatic conditions cannot be cultivated. He suggested that

'It might be possible to lift water for irrigation for starting plantations and to grow trees which require a minimum amount of water. An experiment in this direction may enable the afforestation of the areas which now lie waste, and are classed as culturable but cannot be cultivated.'

Such a scheme would not only result in extending the greatly dwindling forests but also provide grazing area for the cattle and wild herbivores, besides affording much-needed sanctuaries for wild life. In addition, the result of such a scheme of afforestation is sure to help in checking soil erosion and indirectly assist in water conservation through consequent increase in rainfall.

It is essential that similar schemes should be initiated in connection with irrigation plans which, while increasing the area of irrigated lands in the country, have materially influenced the plant and animal life of the streams, rivers, etc. The problems of water conservation in the country are in fact as important as those of the afforestation and conservation of grass-lands, and if these problems are properly tackled, they are sure to go a long way towards the solution of the problems of wild life conservation. Finally, the authorities responsible should see that the recommendations of the Wild Life Conference of 1935 are implemented and carried out as far as possible. Though various provinces are more or less autonomous in regard to the management of the areas under their charge, it should be remembered that wild life conservation in the country cannot be carried out on a provincial basis. The multifarious problems involved cannot be tackled properly until the all-India nature of the problem is realized and a separate department of the Central Government

made responsible for this work. While leaving the local problems to various Provincial Governments and Native States, a central department should be responsible for dealing with the policy of conservation of wild life for India as a whole.

I am afraid, I have given a more or less disjointed picture of a very vast problem. I have tried to indicate that protection of game alone though urgently called for is not enough, and that steps should be taken to draw up and adopt a long-term scheme of wild life conservation as a whole on an all-India basis. Until this is done it will not be possible to preserve and conserve the greatly impoverished wild life of the country.

# THE PLIOCENE-PLEISTOCENE BOUNDARY IN NORTH-WESTERN INDIA

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## ABSTRACT

Recent work in the area between Kashmir Himalayas and the Salt Range, a terrain of most copious sedimentation, reveals no unconformity or palaeontological gap of any significance between late Tertiary and Pleistocene. On the contrary, the voluminous series of fresh-water and subaerial deposits of the Siwalik system, 17,000 feet thick there, bridge the gap, on the whole uninterruptedly, from the Middle Miocene to the lower part of the Pleistocene. The main unconformity of the area is post Upper Siwalik, Lower Pleistocene at the earliest, but this too is not a *hiatus* of any regional importance as it tends to diminish in the Soan valley. From the palaeontological work of Pilgrim (1911-39), detailed field work of the present writer (1921-25) and of G de P Cotter (1926-28) little doubt remains that the Upper Siwalik, except perhaps in the very topmost zone, is pre-glacial and lies astride the Pliocene-Pleistocene boundary. Two type areas of Pliocene-Pleistocene deposits are described (i) the North-West limb of the Soan Synclinal, and (ii) the North East slopes of the Pir Panjal range of Kashmir, in relation to the geotectonic history of North-West India during the Pliocene-Pleistocene interval—the period of maximum uplift of the Himalayas.

## INTRODUCTION

Recent work in the north-western corner of India, between Salt Range mountains and the foot of the Hazara—Kashmir Himalayas—a terrain of most copious sedimentation, reveals, except for a few minor and local breaks, no unconformity or palaeontological gap of any significance between the late Tertiary and Pleistocene. On the contrary, the voluminous series of fresh-water and subaerial deposits (the Siwalik system, 17,000 feet thick) bridges the gap, on the whole uninterruptedly, from Middle Miocene to Lower Pleistocene. A number of small breaks and discordances, due to contemporaneous erosion, do occur in the sequence, as indeed one would expect in a zone of active aggradation by the vigorous repeatedly rejuvenating streams descending from a tract of recent elevation. The Middle and Upper Siwalik series (Pontian to Lower Pleistocene) are strongly developed and are capable of more or less precise division into stages by means of the locally abundant mammalian fauna. The Middle Siwalik (Upper Miocene-Mid Pliocene), broadly speaking, grades off into the Upper Siwalik without any but a few minor breaks which, however, are sporadic and disappear laterally. The main unconformity of the area is post-Upper Siwalik denoted by an unconformable overlap between the Upper Siwaliks and their overlying sub-recent river alluvia. But this too is not a *hiatus* of any regional importance, tending to diminish in the

Soan valley At least 10,000 feet of sediments intervene between the Dhok Pathan stage (Pontian) of the upper Mid Siwalik and the Boulder-Conglomerate stage, the topmost stage of the Upper Siwalik in the Soan valley (a tributary of the Indus) From the palaeontological work of Pilgrim in this area based on more than two decades of research on the fossil bovids, pigs, giraffes and carnivores (1911-39) generally corroborated by detailed field-geological mapping of G. de P. Cotter in the years 1926-28 and of the present writer during 1921-25, little doubt now remains that the Upper Siwalik, except perhaps in the very topmost zone, is pre-glacial and lies astride the Pliocene-Pleistocene interval of Europe Indeed the upper Mid Siwaliks and Upper Siwaliks, from Lower Pliocene upwards, have been grouped together into one unit by more than one observer from the difficulty of separating them by a definite geological dividing line

#### AREAS OF PLIOCENE-PLEISTOCENE DEPOSITS

##### (1) *Sections on the North-Western Limb of the Soan Syncline (Rawalpindi district)*

Clear sections of Upper Tertiary systems of Northern India showing transitional passage into the Quaternary are exposed in the north-western limb of the wide synclinal fold in the Soan valley, Rawalpindi district Incidentally these sections are of importance as representing in a straightforward manner the tectonic history of North-Western India from the beginning of the Tertiary to recent times The field geology of the area was mapped by the present writer on the 1-inch scale in 1921-24 Previous to that A. B. Wynne had mapped the country on 8 miles = 1 inch scale in 1870's The table on the opposite page is a generalised section of the rock sequence, well seen near Gorakhpur on the northern bank of the Soan, 9 miles S S W of Rawalpindi

Lying in a piedmont belt of slow subsidence, *pari passu* with the rising mountains to the north, the Middle and Upper Siwalik strata of the Soan basin show a great deal of folding and deformation, being for considerable stretches vertical in their attitude, or even slightly overfolded at places From vertical dip there is a gradual decrease in the angle of inclination towards the central part of the syncline, the dip flattening to 8°-10°, where the Boulder-Conglomerate stage passes into the older alluvium and from thus to horizontality in the newer alluvium, loess and surface gravels In the area to the east and west of the central Soan basin, the junction between the Boulder-Conglomerate and the older alluvium is unconformable, due to a rapid overlap, the discordance increasing with distance.

W. D. Mathew (1929), De Terra (1939), Colbert (1935) and G. E. Lewis (1937) are inclined to regard the Boulder-Conglomerate as of the Middle Pleistocene age and De Terra takes a conglomerate beneath the Tatrot as denoting a line of unconformity and places the base of the Upper Siwaliks so high up as the boundary between the Pliocene and Pleistocene Apart from the fact that

TABLE OF FORMATIONS IN THE SOAN SECTION

AGE	FORMATION	THICKNESS
RECENT AND SUB-RECENT	Residual gravel-cap, modern alluvia, loess, deeply worn subaerially into labyrinthine ravines <i>Fossils</i> living species Many human artefacts	500-800 ft
MID AND UPPER PLEISTOCENE	Silty clays of warm red colours, gravel and pebbly grit, locally conglomeratic Synclinally inclined $8^{\circ}$ - $10^{\circ}$ <i>Fossils</i> Scarce <i>Elephas</i> , <i>Canis</i> , <i>Bos</i> , many palaeoliths	variable
LOWER PLEISTOCENE TO UPPER PLIOCENE	<i>Boulder Conglomerate and Tatrot stages</i> Conglomerates, coarse pebbly grit, sand-rock and thick earthy clays of red and drab colours Stages represented Tatrot to Boulder Conglomerate Pin for stage not clearly divisible <i>Fossils</i> <i>Swatharium</i> , <i>Cervus</i> , <i>Rhinoceros</i> , <i>Sus</i> , <i>Bos</i> , <i>Equus</i> , <i>Elephas</i> , <i>Hippopotamus</i> , <i>Hyaena</i>	5,700-6,000 ft.
PONTIAN AND SARMA-TIAN	<i>Dhok Pathan stage</i> Soft pebbly sandstones, harder scarp-forming sandstones, pale grey and micaceous, interbedded with few shales of red, orange and drab colours Bands of concretionary clay pseudo-conglomerates <i>Fossils</i> <i>Hipparion</i> , <i>Mastodon</i> , <i>Bramatherium</i> , <i>Helladotherium</i> , <i>Tragocerus</i> and many antelopes, Anthropoid apes	4,000 ft

the basal Tatrot conglomerate of Attock area is an intraformational conglomerate of local occurrence, disappearing laterally, e.g. in the Soan basin, this view has no support from the fossil fauna of the Tatrot stage which, as Pilgrim has shown, is considerably older than Pleistocene. Quite a large number of species as well as genera, including *Hipparion*, have passed upwards from the underlying Dhok Pathans of Pontian age into the Tatrot, while genera such as *Equus* and *Elephas* are rare. While minor unconformities due to contemporary erosion are observed at various levels no important stratigraphic hiatus can be made out between the Middle and Upper Siwalik of the Potwar area as a whole. Such minor breaks and interruptions must be a common feature in a thick fluvial-cum-subaerial series laid down during a period of great earth disturbances. Lateral variation is a universal feature of the Siwaliks, it being a matter of common observation that a fairly wide lens of conglomerate strata traced laterally thins out into a sandstone or grit stratum or even may be replaced by thick beds of clay on either side. A number of small

local breaks and discordances, due to contemporaneous erosion, do occur in the sequence and make, at a few localities, a striking show, as indeed one would expect in a zone of active aggradation by the vigorous, repeatedly rejuvenated streams descending from a mountain-range of recent uplift. But these local unconformities soon tail off in all directions. A geologist working at isolated centres in the Siwalik terrain will naturally place a great deal of emphasis on such minor erosional unconformities and conglomerates met with in the Dhok Pathan, Tatrot and Pinjor stages.

(ii) *The North-East Slopes of the Pir Panjal Range (Kashmir)*

This area also furnishes pertinent evidence on the nature of the boundary under discussion. The Pir Panjal is a sharply defined and individualised tectonic range of the middle Himalayas, separating the foot-hills and plains of the Punjab from the higher ranges of Kashmir. On the gently-sloping north-east face of the range (west flank of Kashmir valley) there occurs, overlying the eroded Mesozoic Himalayan formations, thick sheets of unconsolidated fluvial, lacustrine and glacial deposits (Karewa series) extending from a height of 11,500 feet down to a level of 5,200 feet, which have all but concealed the solid geology of this face of the mountains. In these, the passage of the pre-glacial river and lake-formed beds to those containing the debris of the earlier glaciations is so gradual that it is impossible to draw a dividing line. Moreover it is not definitely known that the onset of the Ice Age in South Kashmir was coeval with the beginning of the Pleistocene, or, as seems more probable, was deferred to a somewhat later date. At a level of about 5,500 feet above the base of the Karewa series a conspicuous erosional unconformity is observed, marked by a bouldery or conglomeratic horizon resting on the denuded edges of folded Lower Karewa beds. The stratigraphical horizon of these boulder-beds, from their contained fossil plants of living species, *Elephas* bones and teeth and some human implements could not be lower than Middle Pleistocene. De Terra regards these boulder-beds as making the second interglacial stage. The lower, more folded and disturbed Karewa beds are also fossiliferous at various localities and horizons throughout their thickness of 5,500 feet though no distinctive remains of chronological value have been found, the fossils being well-preserved leaves, fruits and seeds mostly of dicotyledon plants.

The unconformity mentioned above divides the Karewa series into two unequal divisions. The Lower Karewas, commencing with non-glacial basal pebble-beds, blue, buff and grey clays and sands, succeeded by silts, varved clays, lignite beds and silts interbedded with moraines of the first and second glacial stages (De Terra). The unconformity at the top of the Lower Karewas represents an erosive interval during which over 2,000 feet of the Lower Karewas were denuded from the crests of two prominent anticlines into which they are folded. The stratigraphic level of this unconformity appears to be between the

Lower and Middle Pleistocene and is therefore contemporaneous with the slight stratigraphic break above the Boulder-Conglomerate horizon in the Potwar on the southern side of the Pir Panjal range. The Upper Karewas are about 1,000 feet thick, almost wholly composed of the glacial wash and coarser morainic debris of the third and fourth glaciations, Middle Pleistocene, intercalated with the clay and marl deposits of the lake which intermittently filled the upper Jhelum valley of Kashmir during a large part of the Pleistocene.\* Valuable pioneering work in the glacial succession as recorded in the Karewas and in the river-terraces of Kashmir has been done by De Terra during late years, but considerable detailed and systematic investigation remains to be done in the earlier Pleistocene and late Pliocene of Kashmir.

#### GEOTECTONIC HISTORY OF NORTH-WESTERN INDIA DURING THE PLIOCENE-PLEISTOCENE

The period immediately succeeding the Tertiary was a period of intense orogenic activity in North-West India, it being the final phase of the uplift of the Himalayas, during which, to judge from various evidences observed in the Pir Panjal, the Kashmir Himalayas were uplifted from 5,000–8,000 feet. The tilting and folding of the river and lake-formed Karewas with the fossil plants, fish, batrachians, *elephas*, *rhinoceros*, and a few human implements, and their extension to altitudes up to 11,500 feet, afford a rough estimate of the extent of the movements and of their time duration.

The same conclusion is suggested by the Soan sections of the Potwar on the Punjab side of the Pir Panjal. From the vertically inclined Dhok Pathan and Upper Siwaliks there is seen a gradual decrease in the amount of inclination into the overlying, almost horizontally reposing Soan alluvium. Here every stage is well dated from *Hipparion* to *Equus*, *Mastodon* to *Elephas* and man's traces occur in the topmost disturbed beds. An important chapter in the orogenic history of late Tertiary and early Quaternary time is thus recorded in the Pliocene-Pleistocene formations lying on either side of this interesting Kashmir range, and yet these piedmont formations record no unconformities. The successive orogenic upheavals, instead of interrupting, seem to have accentuated sedimentation in the sub-montane troughs which were being depressed complementary to the rising mountains.

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AN ACCOUNT OF THE CHONDROCRANIUM OF *RANA AFGHANA*  
AND *MEGOPHRYS*, WITH A DESCRIPTION OF THE  
MASTICATORY MUSCULATURE OF SOME TADPOLES

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INTRODUCTION

In another paper (Ramaswami, 1941), I described the chondrocranium of two torrent-dwelling tadpoles, viz, *Heleophryne* and a 'Cystignathid' frog\*. It was concluded there that on account of various dissimilar features, the 'Cystignathid' tadpole showed no resemblance with *Heleophryne* at all, except in a few external characters.

In this short paper, besides describing the salient features in the chondrocranium of the mountain-brook tadpoles of *Rana afghana* (Gunth), *Megophrys parva* (Blgr) and *Megophrys robusta* (Blyth), I propose to describe the masticatory musculature of *Heleophryne* and the 'Cystignathid' tadpole and also the muscles connected with the suctorial apparatus of these forms. For purposes of comparison, I have studied tadpoles of *Microhyla* (Microhylidae) and several species of *Rana* also.

In my previous papers (Ramaswami, 1940, 1941, 1941a) the historical account of work done on the chondrocranium of anuran tadpoles has been detailed. While a large number of papers has been published on land chondrocranium (Parker, 1871, 1881, Stöhr, 1881, Gaupp, 1893, Spemann, 1898, Peeters, 1910, de Beer, 1937 and Pusey, 1938) there is only one account by Kruijtzter (1931) on *Megophrys montana* (Kuhl).

MATERIAL

I am very grateful to Dr. S. L. Hora of the Zoological Survey of India for making available some stages of the tadpoles of *Megophrys parva* and *Megophrys robusta* and a stage of *Rana afghana*. I am also thankful to Mr. J. L. Bhaduri for sending me some tadpoles of *M. parva*, and to the Director, Zoological Survey of India, for an adult specimen of *Rana afghana*. I wish to express my sincere thanks to Prof. A. Subba Rao for helpful criticism.

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\* Annandale and Hora (1922) described a tadpole from the hills of Cochin, India, as resembling that of *Heleophryne* and, therefore, assigned it to the Cystignathid family, the adult of which is still unknown. I have called this tadpole a 'Cystignathid' tadpole.

The following stages of the tadpoles have been studied.

- 1 *Rana afghana* (Günth) (2 limbed), total length 51 mm., head and trunk 18 mm
- 2 *Megophrys parva* (Blgr) (premetamorphic stage)
  - Stage A—total length 25 mm, head and trunk 9 mm
  - Stage B—total length 34 mm, head and trunk 10 mm
  - Stage C—total length 55 mm, head and trunk 14 mm. (metamorphosing tadpole, 4 limbed)
- 3 *Megophrys robusta* (Blyth) (premetamorphic stage), total length 39 mm, head and trunk 11 mm

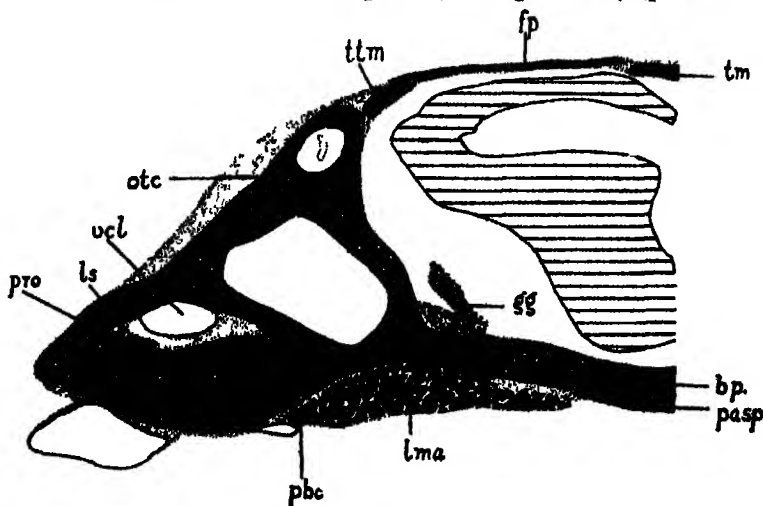
#### OBSERVATIONS

##### *Rana afghana* (Günth) (51 mm premetamorphic stage)

I shall restrict myself to the very important features noticed in the various regions of the chondrocranium since they resemble those of a ramid tadpole very closely

*Occipitoauditory region* The notochord is present on the ventral aspect of the basal plate and anteriorly becomes wedge-shaped. An operculum is noticeable. A tectum synoticum is developed in the roof.

An interesting feature is noticed in this region. The pterygoquadrate unites with the base of the otic capsule (text-fig. 1, *otc*) (posterior to the



TEXT FIG. 1.—Transverse section of *R. afghana* in the region of otic connection,  $\times 24$ .

*bp*, basal plate, *fp*, frontoparietal; *gg*, gasserian ganglion, *lma*, M levator m. anterior; *ls*, M levator m. posterior superficialis, *otc*, otic capsule, *pasp.*, parasphenoid, *pbc.*, pseudobasal connection, *pro.*, otic connection, *tm*, taenia medialis; *tmm.*, taenia tecti marginalis, *vcl*, vena capitis lateralis

facial nerve) forming a pseudobasal connection (*pbc*) and dorsally it unites with the crista parotica forming the otic connection (*pro*) The head vein (*vcl*) runs in the cranio-quadrato passage

**Orbitotemporal region** The processus ascendens is prominently present and this bears the typical relation with the pila antotica and with the branches of the trigeminal nerve The side of the cranium is formed as in *Rana* (de Beer, 1937)

**Ethmoid region** A pseudopterygoid process is wanting, anteriorly the quadratocranial commissure bears the processus quadrato-ethmoidalis which forms the quadrato-ethmoidal connection with the processus lateralis of the trabecula The cornua trabeculae are short, thick and broad The supra-rostral is large and powerfully built The cartilages supporting the olfactory chambers are not formed The infrarostrals are connected together by basimandibular and each is connected with Meckel's cartilage of its side by procartilaginous cells

**Ossification** Frontoparietal (text-fig 1, *fp*) and parasphenoid (*pasp*) bones are noticed

*Megophrys parva* (Blgr) Stage A, 25 mm, Stage B, 34 mm., premetamorphic stages

*Megophrys robusta* (Blyth)—39 mm, premetamorphic stage

**Occipitoauditory region** The notochord is wedge-shaped and is not included dorsally and ventrally by cartilage A tectum synoticum is not developed in both species Two acoustic foramina (median and posterior) are noticed in both species No operculum is developed An otic connection is absent

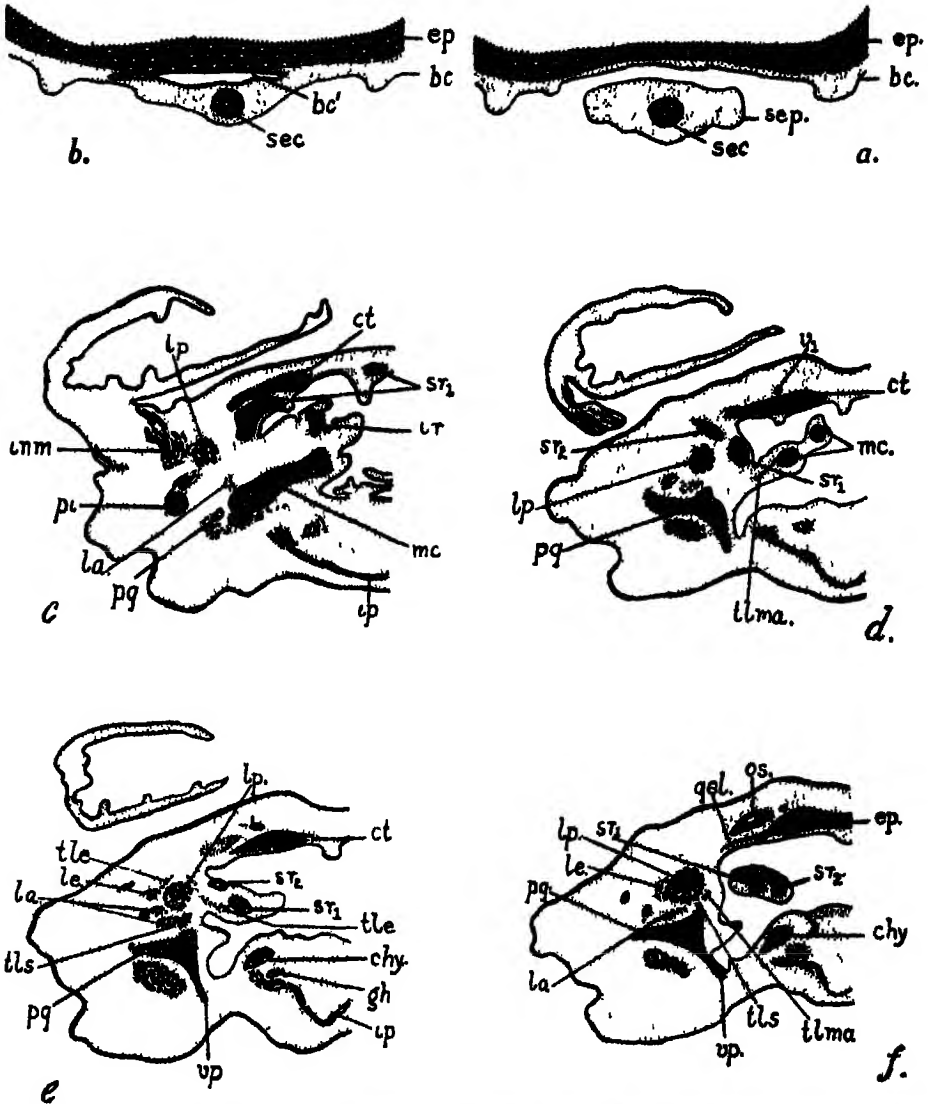
**Orbitotemporal region** In stage A of *M. parva*, a hypophysial fenestra is present, while in stage B of the same and in *M. robusta*, the fenestra is absent

There is an interesting feature in this region of the tadpoles of *M. parva* examined There is a tongue-like projection from the roof of the buccal cavity (text-figs 2a, 2b) anteriorly in stage B, this is supported by a cartilaginous piece I have called these the subethmoidal process (*sep*) and cartilage (*sec*) respectively In stage A this subethmoidal process is noticed but is not supported by a cartilage. In *M. robusta* again, the arrangement is as in stage A of *M. parva*

In both species the ventral process from the pterygoquadrato (Pl. I, figs. 1, 2, *pv* and text-figs. 2e, 2f, *vp*) and the processus infundibularis (Pl. I, figs. 1, 2 and text-fig. 2c, *pi*.) from the anterior end of the pterygoquadrato are conspicuously present

The lateral process from the trabecula gives rise to the quadrato-ethmoidal ligament (text-fig. 2f, *gel*.).

As in *M. montana* (Kruijtz, 1931) there are two pairs of suprarostrals (text-figs. 2c, 2d, 2e, 2f, *sr*<sub>1</sub>., *sr*<sub>2</sub>.). Suprarostal 1 is large (Pl. I, figs 1, 2,



TEXT FIGS 2a, 2b, 2c, 2d, 2e and 2f—Transverse sections of *Megophrys parva* in the subethmoidal cartilage region (2a, 2b,  $\times 50$ ) and in the region of upper and lower jaws (2c anterior and 2f posterior,  $\times 25$ ).

bc, buccal epithelium; bc', buccal cavity; chy, ceratohyal; ct, cornua trabeculae; ep., ethmoid plate; gh, M. geniohyoideus; lnm, M. infundibularis; lr, infrarostral; lp, M. intermandibularis posterior; la, M. levator m. anterior articularis; le, M. levator m. externus; lp, M. levator m. posterior profundus; mc., Meckel's cartilage; os, olfactory sac; pl., processus infundibularis; pq, pterygoquadrate; qel, quadrato-ethmoidal ligament; sec, subethmoidal cartilage; sep., subethmoidal process; st<sub>1</sub>, st<sub>2</sub>, suprarostral 1 and 2; tle, tendon of M. levator m. externus; tle., tendon of M. levator m. anterior; tle., tendon of M. levator m. posterior superficialis; up., processus ventralis; v<sub>1</sub>, r. ophthalmicus profundus V

$sr_1$ ), articulating ventrolaterally on either side of the ends of cornua trabeculae, proceeds posteriorly under the lateral portion of the cornua as a rodlike structure ( $sr'_1$ ). The suprarostral 2, starting as a piece of cartilage articulating with the lateral aspect of the cornua trabeculae, proceeds internally and embraces as a semicircle the rod-like portion of the suprarostral 1.

*Megophrys parva* (Blgr) Stage C, 55 mm, metamorphosing stage

**Occipitoauditory region** The notochord is surrounded on all sides, except ventrally, by the parachordal. A tectum synotium and an operculum have appeared. Three acoustic foramina are present. The foramen acousticum medium and posterior are noticed together and the anterior in the region of the ductus endolymphaticus.

**Orbitotemporal region** The processus ascendens has broken down. A carotid foramen is absent and in the region of the oculomotor foramen the hypophysial artery becomes intracranial through the oculomotor foramen. Anterior to the metoptic foramen the pila metoptica is indicated in the form of a slight elevation from the trabecula, which does not reach the orbital cartilage. Therefore, there is no true pila metoptica.

**Ethmoid region** The suprarostral and quadratocranial commissure have broken down. The cartilages of the nasal region are well developed.

**Ossification** While in *M. robusta* a parasphenoid is developed, in *M. parva* it is absent.

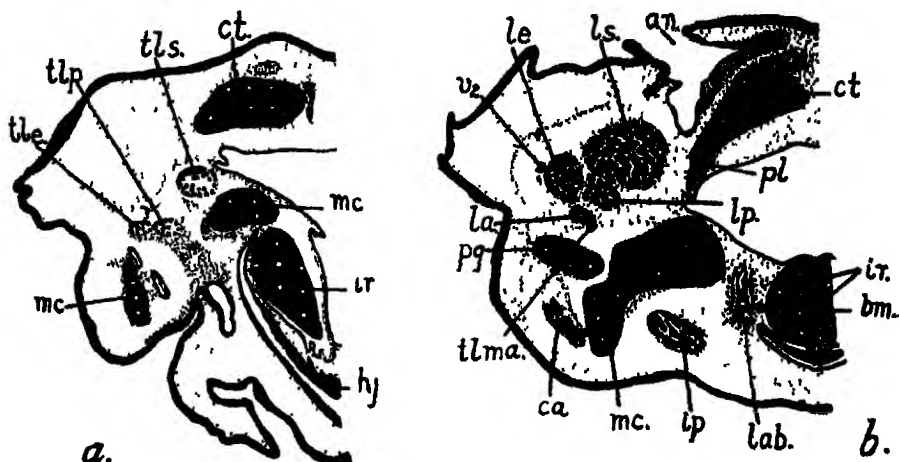
#### *Masticatory muscles.*

##### 1. Levator mandibulae posterior superficialis (Edgeworth, 1935)

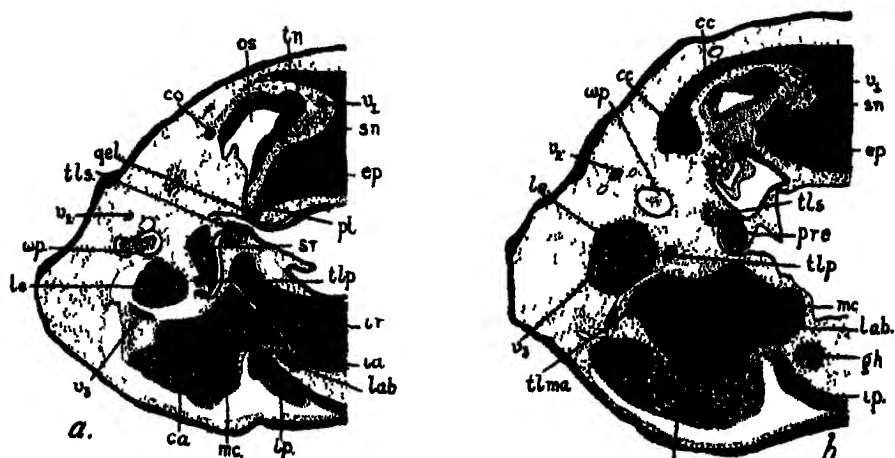
This muscle arises from the processus ascendens and the pterygoquadrate fanwise and has its tendon (text-figs 3a, 3b, *ils*, *ls*) inserted on the inner aspect of Meckel's cartilage in *Rana hexadactyla* Lesson, *R. cyanophlyctis* Schneid., *R. afghana*, *Heleophryne*, *Microhyla* and the 'Cystignathid' tadpole. In *R. tigrina* Daud. (text-figs 4a, 4b), peculiarly the tendon (*ils*) is inserted on infrarostral ( $sr$ ), a feature in which it stands apart from other tadpoles.

##### 2. Levator mandibulae posterior profundus (Edgeworth, 1935)

Arising similarly as the above but below it in position, this muscle has its tendon inserted on suprarostral. In *R. temporaria* (Gaupp, 1893), a part of the tendon is inserted on Meckel's cartilage while the main one is on suprarostral. In *R. tigrina* the smaller portion is lost in the connective tissue near Meckel's cartilage; the longer (text-fig. 4a, *llp*) gains attachment on suprarostral ( $sr$ ). In *R. cyanophlyctis*, *R. hexadactyla*, *Heleophryne* and the 'Cystignathid' tadpole, the large tendon is inserted on suprarostral; in *Megophrys*, it is on suprarostral 1. In *Microhyla* the tendon is noticed posterior to the origin of *l.m. externus*. In *Pelobates* Schulze (1892) found a single insertion, while Luther (1914) described two as in *R. temporaria* (Gaupp, 1893).



TEXT FIGS 3a, 3b —Transverse sections in the anterior region of *R. hexadactyla*,  $\times 20$   
 an, anterior naris, bm, basimandibular, ca, M ceratohyoangularis, ct., cornus trabeculae,  
 hy., horny lower jaw, lp, M intermandibularis posterior, tr, infrarostral, la, M levator  
 m. anterior articularis, lab, M mandibulolabialis, le, M levator m. externus, lp, M  
 levator m. posterior profundus, ls, M levator m. posterior superficialis, mc, Meckel's  
 cartilage, pl, processus lateralis, pg, pterygoquadrate, tle, tendon of levator m. externus,  
 tlma, tendon of M levator m. anterior, tlp, tendon of M levator m. posterior profundus,  
 tle, tendon of M levator m. posterior superficialis, v<sub>3</sub>, r maxillaris V



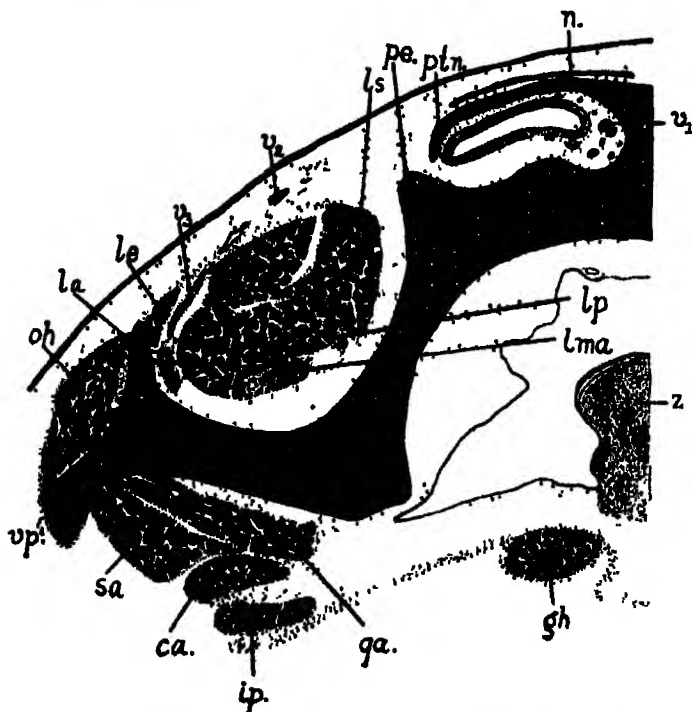
TEXT FIGS 4a, 4b —Transverse sections in the anterior region of *R. tigrina*,  $\times 21$ .  
 ca, M ceratohyoangularis, cc, commissural cartilage, co., cartilago obliqua; ep., ethmoid  
 plate, gh., M geniohyoideus; la., M intermandibularis anterior; ep., M. intermandibularis  
 posterior, tr, infrarostral, lab, M mandibulolabialis, le, M. levator m. externus, ce.,  
 olfactory sac, pl., processus lateralis, pre., processus quadrato-ethmoidalis, qel, quadrato-  
 ethmoidal ligament, sn, septum nasi; sr., suprarostral; tlma., tendon of M. levator m.  
 anterior, tlp, tendon of M levator m. posterior profundus; tle, tendon of M. levator m.  
 posterior superficialis, tn, tectum nasi; v<sub>1</sub>, v<sub>2</sub>, v<sub>3</sub>, the three branches of trigeminal nerve;  
 wp, worm parasite

In *Xenopus* (Edgeworth, 1935, Paterson, 1939) the levator mandibulae posterior is not differentiated into superficial and deeper parts, the muscle extends from the posterior part of processus muscularis

### 3 Levator mandibulae anterior (Edgeworth, 1935)

This muscle arises invariably from the base of the otic capsule and the tendon is inserted on the external aspect of Meckel's cartilage (text-figs 3b, 4b, 5lma), this is seen in *R. cyanophlyctis*, *R. hexadactyla*, *R. tigrina* and the 'Cystignathid' tadpole. In *Megophrys* it arises from the ventral aspect of processus ascendens, in *Heleophryne* the origin is from the pseudobasal process before the latter unites with the cranium

In *Xenopus* (Edgeworth, 1935, Paterson, 1939) this muscle arises posteriorly to *lm* posterior on the subocular bar of the pterygoquadrate and is dorsal to the latter muscle

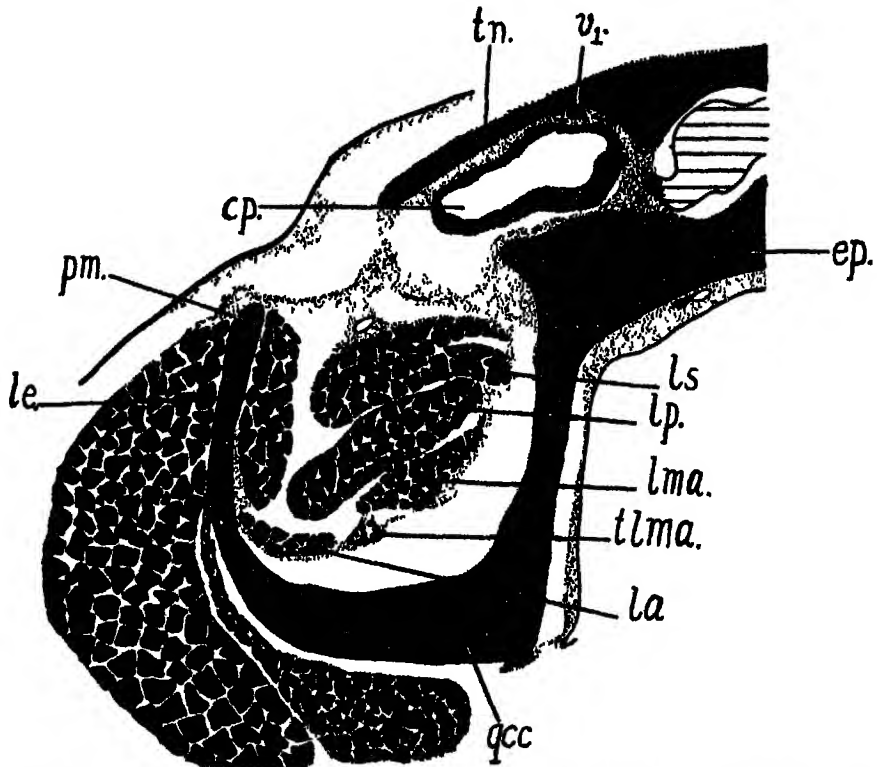


TEXT-FIG. 5.—Transverse section of the 'Cystignathid' tadpole in the quadratocranial commissure region,  $\times 30$ .

ca, M. ceratohyoangularis; gh, M. geniohyoideus, lp, M. intermandibularis posterior, la., M. levator m. anterior articularis, le, M. levator m. externus, lma, M. levator m. anterior; lp, M. levator m. posterior profundus, ls, M. levator m. posterior superficialis, n, nasal; oh, M. orbitohyoideus, pe, pila ethmoidalis, ptn, posterior portion of tectum nasale; qa., M. quadratoangularis; sa, M. suspensorioangularis, vp', ventral process, v<sub>1</sub>, v<sub>2</sub>, v<sub>3</sub>, branches of the trigeminal nerve; z, tongue

## 4 Levator mandibulae externus (Edgeworth, 1935).

This muscle arises (text-figs 5, 6, 7, *le*) from the inner aspect of the processus muscularis and inserts by a tendon on suprarostral (text-fig 2*e*, *tle*) In *Microhyla*, where the processus muscularis is not prominent, the muscle (text-fig 7, *le*) arises from the external aspect of the pterygoquadrate. The tendinous insertion may be separate from that of *lm* posterior profundus (*Megophrys* suprarostral 1, *Rana*) or united as in the 'Cystignathid' tadpole and *Heleophryne*. In *Microhyla* I was not able to discover a tendon, for the muscle shows itself by the side of suprarostral from the very anterior sections.



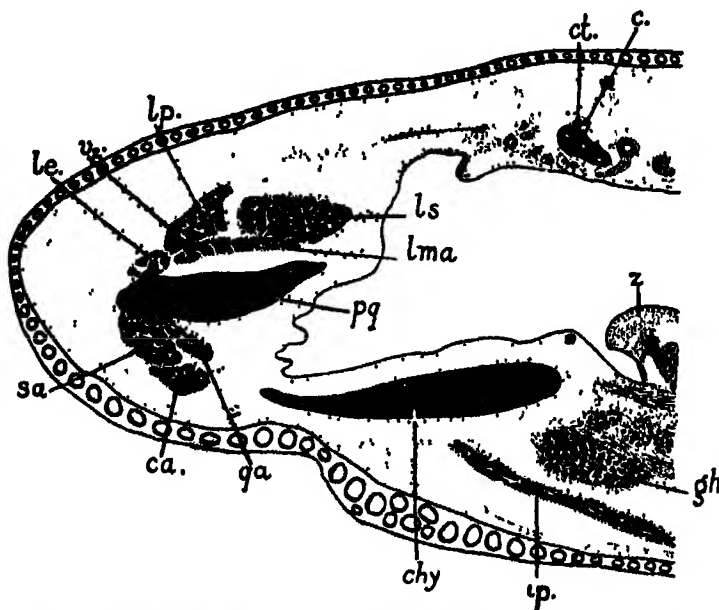
TEXT FIG 6.—Transverse section of *R. afghana* in the region of processus muscularis,  $\times 30$  *cp.*, cavum nasale principale, *ep.*, ethmoid plate, *ls.*, M levator m. anterior articularis, *le.*, M levator m. externus, *lp.*, M levator m. posterior profundus, *ls.*, M levator m. posterior superficialis, *lma.*, M levator m. anterior, *qcc*, quadrato-orbital commissure; *pm.*, processus muscularis, *tlma.*, tendon of M. levator m. anterior, *tn.*, tectum nasi; *v1.*, r ophthalmicus profundus V.

## 5 Levator mandibulae anterior articularis (Edgeworth, 1935)

This muscle arises (text-figs. 5, 6, *la.*) below *lm*. externus inside the processus muscularis and inserts directly on Meckel's cartilage and the tendon,

if present, is extremely short Only in *Microhyla* I was not able to note the presence of this muscle

The levator mandibulae anterior lateralis (*R. temporaria*, *Pelobates*; Luther, 1914) and the levator mandibulae anterior subexternus (*Pelobates*; Luther, 1914) are absent in the tadpoles examined by me Probably the *lm* anterior subexternus is merged with *lm* externus



TEXT-FIG 7—Transverse section in the anterior region of *Microhyla ornata*,  $\times 80$

*c*, cartilage, *ca*, M. ceratohyoangularis, *chy*, ceratohyal, *gh*, M. geniohyoideus, *le*, M. levator m. externus, *lp*, M. levator m. posterior profundus, *lma*, M. levator m. anterior, *ls*, M. levator m. posterior superficialis, *pq*, pterygoquadrate, *qa*, M. quadratoangularis, *sa*, M. suspensorioangularis, *sh*, M. interhyoideus, *v<sub>2</sub>*, r. maxillaris V, *z*, tongue

### Muscles of the oral sucker

#### 1 Intermanibularis anterior (Edgeworth, 1935)

In *R. afghana*, arising from Meckel's cartilage and inserted into the median portion of the posterior lip, is a muscle called *A* (Bhaduri, 1935), which is considered to be a modified M. intermandibularis anterior In the 'Cystignathid' tadpole, *R. hexadactyla* and *Heleophryne* the muscle is wanting, in *R. tigrina* (text-fig. 4a, va), *Microhyla* and *Megophrys* it is present and runs between the two infrarostrals as in *Pelobates* (Luther, 1914)

#### 2. Mandibulolabialis (Edgeworth, 1935)

In *R. afghana* (Bhaduri, 1935) this muscle goes into the lower lip fanwise from Meckel's cartilage; similarly, it is noticed in the 'Cystignathid', *Heleo-*

*phryne*, *R. tigrina* (text-fig 4b, lab) and *R. hexadactyla* (text-fig 3b, lab) tadpoles. In *Microhyla* and *Megophrys* it is absent. Probably in *Megophrys* the infundibular muscles are modified M mandibulolabials (see below).

### Special muscles

In *R. afghana*, Bhaduri (1935) described a muscle *C*, which finds a probable homologue with the M diaphragmatobranchialis medialis of Schulze (1892). According to him this muscle arises from the skin posterior to the diaphragm and passing through the same is inserted to the ceratobranchial cartilage. Edgeworth (1935) considers this as M rectus cervicis. Bhaduri also described a muscle *E*, which he considered to be modified, arising from the diaphragm and inserting into a 'cartilage in the exoccipital region'. A probable homology with M diaphragmatobranchialis lateralis (Schulze, 1892) was noted. However, this muscle—diaphragmatobranchialis IV (Edgeworth, 1935) in *Pelobates*—arises from the diaphragm and is inserted to the ceratobranchial cartilage. In the 'Cystignathid' tadpole, the M rectus cervicis arising from the diaphragm, running by the side of the heart is inserted on the ceratobranchial cartilage. In *Heleophryne* this muscle arises from the ventral skin and is inserted to the ceratobranchial, it is short.

Mention must be made of the infundibular muscles of *Megophrys* (text-fig 2c, *imm*). They arise from the infundibular process of the pterygoquadrate and spread into the lower lip, probably these are modified mandibulolabialis muscles.

### DISCUSSION

The salient features in the organisation of the chondrocranium of the torrent-dwelling *R. afghana* and *Megophrys* can now be enumerated and compared with those in *Heleophryne* and the 'Cystignathid' tadpole which also inhabit similar brooks.

In *R. afghana*, in the occipitoauditory region, a tectum synoticum is developed as in other genera, viz., *Rana*, *Bufo* (Parker, 1871, 1876), *Pelobates* (Schulze, 1892), *Alytes* (van Seters, 1922), *Polypedates* (Okutomi, 1937), *Rana* (de Beer, 1937), *Xenopus* (Paterson, 1939), *Calyptocephalus* (Reinbach, 1939), *Microhyla* and *Uperodon* (Ramaswami, 1940). In *Heleophryne* it is absent while in the 'Cystignathid' tadpole it is developed (Ramaswami, 1941). In the metamorphosing stage of *M. parva* it has appeared. According to Kruijtzter (1931) it is noticed in *M. montana* that 'the tectum posterius originates in two phases, the anterior part before metamorphosis, the posterior part during metamorphosis'. I have observed the occurrence of a tectum synoticum only in stage C of *M. parva* and whether it makes its appearance prior to this can only be settled by an examination of the intervening stages.

The otic connection of the pterygoquadrate with the crista parotica is not uniformly met with. In *Alytes* (van Seters, 1922), *Megophrys* (Kruijtzter, 1931), *Discoglossus* (Pusey, 1938), *Calyptocephalus* (Reinbach, 1939), some

species of *Bufo* (Parker, 1876, Ramaswami, 1940) and *Rana curtipes* (Ramaswami, 1940) the otic connection is absent. However, in one series of *M. montana* tadpoles (series 16) Kruytzer (1931) recorded the occurrence of an otic connection.

*Rana afghana* possesses only two acoustic foramina—*foramen acusticum anterius* and *foramen acusticum posterius*—as in ranids generally. In *M. parva* there are only two acoustic foramina—the foramina *a. medius* and *a. posterior* in stages A and B. In stage C, all the three foramina are formed, the anterior-most appearing just behind the *foramen ductus endolymphaticus*, while the *foramen acusticum medium* and *a. posterior* appear near each other, the former situated ventrally to the latter. Kruytzer (1931) also recorded in series 2 (17 mm) of *M. montana* that 'At first (series 2) these foramina form one whole (fig 4)' and later on the three foramina are formed in the septal wall of the otic capsule. The existence of three acoustic foramina has been reported in a large number of anuran forms (Miyawaki, 1927, 1929, Reinbach, 1939).

The operculum makes its appearance during different stages of development in different tadpoles. The examined stage of *R. afghana* possesses an operculum while only in stage C of *M. parva* it is noticed. Kruytzer (1931) described the appearance of an operculum in a tadpole of *M. montana* measuring 37 mm. In the 'Cystignathid' tadpole prior to metamorphosis, I have recorded (Ramaswami, 1941) the occurrence of an operculum, while the same appeared during metamorphosis in *Heleophryne*.

In the region of the *processus oticus* connection in *R. afghana* the pterygoquadrate unites with the base of the otic capsule forming a pseudobasal connection being posterior to the *r. palatinus facialis*. The *vena capitis lateralis* runs in the cranioquadrate passage between the otic and pseudobasal connections. In the adult this connection breaks down into a pseudobasal articulation. While a pseudobasal connection is formed in *R. temporaria* (de Beer, 1937) only during metamorphosis (20 mm) which later becomes a pseudobasal articulation, in *R. afghana*, long prior to the onset of metamorphosis a pseudobasal connection is formed. In *R. curtipes* (Ramaswami, 1940) I have reported the occurrence of a pseudobasal articulation in premetamorphic tadpole examined. In *Megophrys* (Kruytzer, 1931), however, 'During metamorphosis this ventral process [*processus ventralis capsulae auditivae*] forms a basal articulation with the basal process of the pterygoquadrate (fig 8). After metamorphosis both processes fuse, so that the joint disappears'. Thus, while the chondrocranium is incompletely autostylic, the adult skull is completely autostylic. On the other hand, *Rana afghana* tadpole with the possession of a quadrato cranial, ascendens, otic and pseudobasal connections is typically autostylic and it becomes incompletely autostylic after metamorphosis. The tabular form below shows the arrangement in the two other torrent dwelling forms from which it can be noted that *R. afghana* is the only typically completely autostylic form. Further, *Megophrys*, though a denizen of torrential streams, possesses only two pterygoquadrate connections whereas

common tank-dwellers like *R temporaria*, *R hexadactyla* and *R tigrina* possess three connections, viz, quadratocranial, ascendens and otic.

*Cartilaginous connections of the pterygoquadrate with the cranium before metamorphosis*

	Quadrato- cranial commisure	Ascendens connection	Pseudobasal connection	Otic connection
<i>Rana afghana</i>	present	present	present	present
The 'Cystignathid' tad pole	present	present	absent	present
<i>Heleophryne purcelli</i>	present	absent	present	present
<i>Megophrys parva</i>	present	present	absent	absent

I have not been able to discover in *M parva* (stage C) the pseudobasal process appearing as a procartilaginous *Anlage* independently of the quadrate below the otic capsule as described by Kruytzer (1931) in *Megophrys* and *Alytes*. Pusey (1938) considered this rudiment in *R temporaria* as the basitrabecular process which secondarily gained attachment with the quadrate and later formed the pseudobasal articulation.

The carotid artery becoming intramural through its foramen gives off the ophthalmica magna and palatine arteries. In *Megophrys*, there is no palatine artery, and as in *Rana*, during metamorphosis, the trabecular portion between the carotid and oculomotor foramina breaks down.

Slightly posterior to the ethmoid plate, in stage B of *M parva*, there is a subethmoidal cartilage. This is situated ventrally to the ethmoid plate, and is independent, establishing no connection with any other cartilage. In an earlier stage and also in stage C of the same species this cartilage is absent, in the examined stage of *M robusta*, there is a digitiform process but this is not supported by a cartilaginous core. Such a subethmoid cartilage has not been described in any tadpole so far examined.

A processus quadrato-ethmoidalis is reported to be absent in *M. montana* (Kruytzer, 1931) and *Xenopus* (Kotthaus, 1933, Paterson, 1939). In my sections of *M parva*, I have noticed the quadrato-ethmoidal ligament running from the processus lateralis of the trabecula to the anterior face of the quadratocranial commissure. In *R hexadactyla* (Ramaswami, 1940) I have reported that in the premetamorphic stages, besides a ligamentary quadrato-ethmoidal commissure, there is also a cartilaginous one.

The suprarostral is powerfully built in *R afghana* as in the 'Cystignathid' and *Heleophryne* tadpoles (Ramaswami, 1941). In *Megophrys*, there are two pairs of suprarostals—suprarostral 1 and 2. Kruytzer (1931) also recorded the same in *M montana*. In *Pelobates* (Schulze, 1892; Luther, 1914) the suprarostral 1 is large and crescentic while the suprarostral 2 projects from the

posterolateral face of suprarostrals 1 Some species of *Bufo* (Parker, 1881) have also two suprarostrals

Unlike the 'Cystignathid' and *Heleophryne* tadpoles (Ramaswami, 1941) the processus muscularis is well developed in *R. afghana* and *Megophrys*

From the region of the pars quadrata arises in the two early stages of *M. parva* and *M. robusta* an anterior extension called the processus infundibularis. In my figures muscles associated with this process are also depicted. A similar process is also noticed in *M. montana* (Kruijtzter, 1931). This infundibular process of *Megophrys* supports the lower lip from which arises an extension which along with a modified part of the upper lip goes to form the 'funnel'-shaped mouth so characteristic of these tadpoles. Moreover, in the premetamorphic stages of *Megophrys* examined at the region where the pterygoquadrate gives off the infundibular process, there also arises a ventrally directed process which is called the ventral process. It is free from muscular attachment and extends as far as the anterior region of the articulation of the ceratohyal with the ventral aspect of the pterygoquadrate. Such a process is also described by Kruijtzter (1931) in *M. montana*. These two processes in the stages examined show signs of breakdown during metamorphosis. In *M. montana* (Kruijtzter, 1931) the ventral process 'remains during and after metamorphosis and plays an important part in the formation of the ventral part of the later pars quadrata'.

The development of a complete autosystyly in *R. afghana*, i.e., the attachment of the pterygoquadrate with the cranium in four regions, is peculiar to this and the other two tadpoles, viz., the 'Cystignathid' and *Heleophryne*, lack one or the other connections. But all these are torrent-dwellers. While *Heleophryne* has specialised in the possession of extra cartilages (dorsal rostral and sub-Meckelian) and ligamentary connections (quadrato-otic), the 'Cystignathid' has developed by the widened rostral cartilages, a powerful oral suctorial disc. In *Megophrys* which simply float vertically in water, the infundibular and ventral processes of the pterygoquadrate are developed. Thus each tadpole has specialised in its own way and it is difficult to say which has evolved more suitable adaptations for a life in torrential waters.

In *R. afghana*, the intermandibularis muscle is believed to be so modified that instead of running between the two infrarostrals, arises from Meckel's cartilage and runs into the lower lip. Such a feature is not noticed in the three other mountain brook tadpoles, viz., the 'Cystignathid', *Heleophryne* and *Megophrys*. In fact the muscle is wanting in the two former and *R. hexadactyla*; in *Megophrys* it resembles that of the ranids as described by Luther (1914) and Edgeworth (1935). Further, in *Megophrys* the mandibulolabialis muscle is wanting and instead of this, the infundibular muscles arising from the processus infundibularis spread into the lower lip. In the 'Cystignathid' and *Heleophryne* tadpoles, the mandibulolabialis muscles are well developed.

As regards the M. diaphragmatobranchialis in *R. afghana*, the median (= Rectus cervicis) and lateral (= diaphragmatobranchialis IV) ones are well

developed In both the 'Cystignathid' and *Heleophryne* tadpoles there is only one pair of muscles arising from the skin or diaphragm and ending in the ceratobranchial cartilage—the M rectus cervicis, the diaphragmato-branchialis IV being absent It is clear that in the absence of this lateral diaphragm muscle, which is supposed to create the vacuum necessary for adhesion in these torrent-dwelling tadpoles, some other muscle must be responsible for it

Bhaduri (1935) described in *R afghana* a muscle which he labelled *F* as a modified subbranchial muscle (Schulze, 1892) Edgeworth (1935) in his fig 418 labels the same muscle as interhyoideus posterior but in the table of synonyms (p 271) he homologises Schulze's subbranchialis with constrictor colli This muscle has not been noticed by me in the 'Cystignathid' and *Heleophryne* tadpoles

No muscle enters into the upper lip directly as in the lower, but the upper beak is controlled by the Mm 1 m posterior profundus and 1 m externus which are inserted to the suprarrostral

### CONCLUSION

In the possession of an infundibular process, from which the infundibular muscles originate and spread into the lower jaw, *Megophrys* seems to be well adapted for a floating life No other special modifications are noticed in the chondrocranium *R afghana* seems to be pre-eminently suited for a life in torrential waters, the possession of modified muscles of the sucker and diaphragm and the four connections of the pterygoquadrate with the cranium are characteristic

### SUMMARY

1 In the metamorphosing stage of *Megophrys*, there are three acoustic foramina, in earlier, there are only two

2 In *Megophrys* a processus ascendens is present and an otic connection is absent In *R. afghana* a processus ascendens, otic and pseudobasal connections of the pterygoquadrate are noticed As in ranids, the pseudobasal connection breaks down and the adult has only a pseudobasal articulation

3 In stage B of *M parva* a subethmoidal process is given off from the roof of the mouth into the buccal cavity, this is supported by an independent piece of cartilage

4 A processus quadrato-ethmoidalis is noticed in *M parva*, it is reported to be absent in *M montana*

5 From the region of pars quadrata of *Megophrys*, an infundibular process is given off from which infundibular muscles enter into the lower lip. This process breaks down during metamorphosis

6 No other tadpole shows all the four connections of the pterygoquadrate in premetamorphic stage as is the case in *R afghana*, viz., quadrato-

cranial, ascendens, otic and pseudobasal connections. Thus *R. afghana* is typically completely autosystylic.

7 The modified intermandibular muscle noticed in *R. afghana* is absent in the 'Cystignathid' and *Heleophryne* tadpoles.

8 A diaphragmatobranchialis IV is wanting in the 'Cystignathid' and *Heleophryne* tadpoles.

9 Uniformly all the tadpoles examined by me have the masticatory muscles, viz., levator m. posterior superficialis, l. m. posterior profundus, l. m. externus, l. m. anterior and l. m. anterior articularis, only in *Microhyla* the last one is wanting. The l. m. anterior subexternus and l. m. anterior lateralis are absent in all these. A mandibulolabialis is wanting in *Microhyla* and *Megophrys*. Peculiarly in *R. tigrina*, the l. m. posterior superficialis is inserted to the infrarostral.

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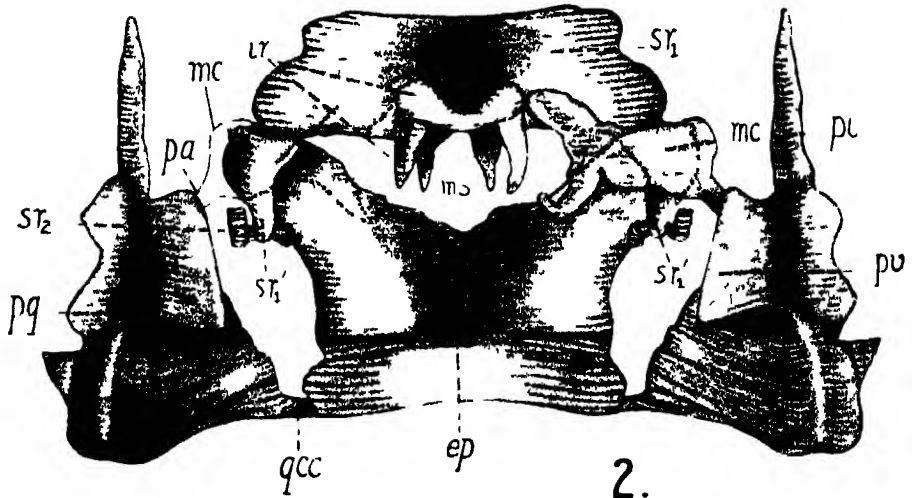
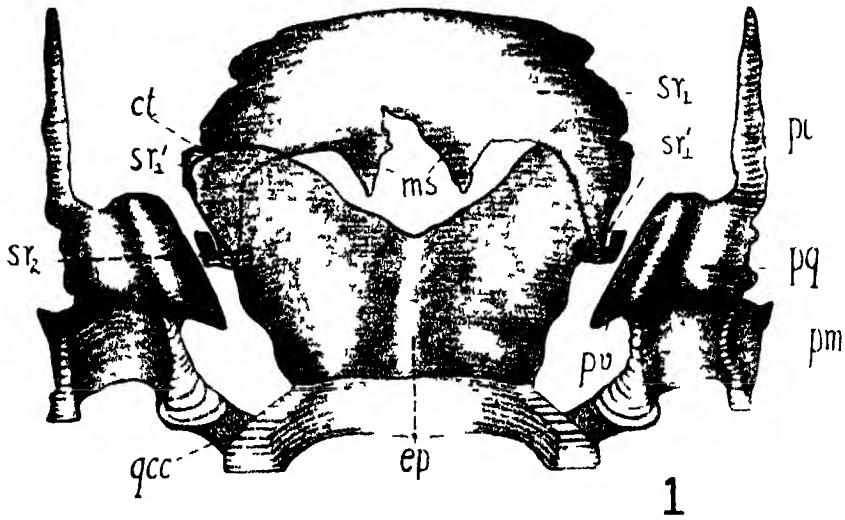


FIG 1 —Dorsal aspect of the anterior portion of the chondrocranium of *Megophrys parva*. Meckel's cartilage and infrarostrals not shown, model,  $\times 50$

FIG 2 —Ventral aspect of the anterior portion of the chondrocranium of *Megophrys parva*, model,  $\times 50$

ct, cornua trabeculae, ep, ethmoid plate, sr, infrarostral, mc, Meckel's cartilage, ms, median posterior portion of suprarostrals 1, pa, pars articularis Meckel's, pv, processus infundibularis, pm, processus muscularis, pq, pterygoquadrate, pv, processus ventralis, qcc, quadratoacranial commissure, sr<sub>1</sub>, suprarostrals 1, sr<sub>2</sub>, suprarostrals 2, sr<sub>1</sub>', posterior portion of sr<sub>1</sub> gaining relation with sr<sub>2</sub>



# GAMETOGENESIS AND EMBRYOGENY OF *EULOPHEA* *EPIDENDRAEA* FISCHER

By B G L SWAMY

(Communicated by Dr P Maheshwari, D Sc , F N I )

(Read October 5, 1942 )

*Eulophea epidendraea* Fischer is a terrestrial orchid, growing wild in the scrub jungles of South India. Of the several genera in the sub-tribe Eulophueae (Tribe Vandae), *Eulophea* is the only genus reported from India (Hooker, 1894).

The vegetative activity of the plant commences soon after the outbreak of monsoons in July. The plant possesses large conical pseudobulbs, which are greenish in early stages and later turn greyish brown, with persistent leaf bases. The inflorescences, usually 1 to 2 per pseudobulb, spring up laterally and attain a length of nearly 3 feet, bearing pale greenish flowers in racemose fashion from September to December.

## Flower

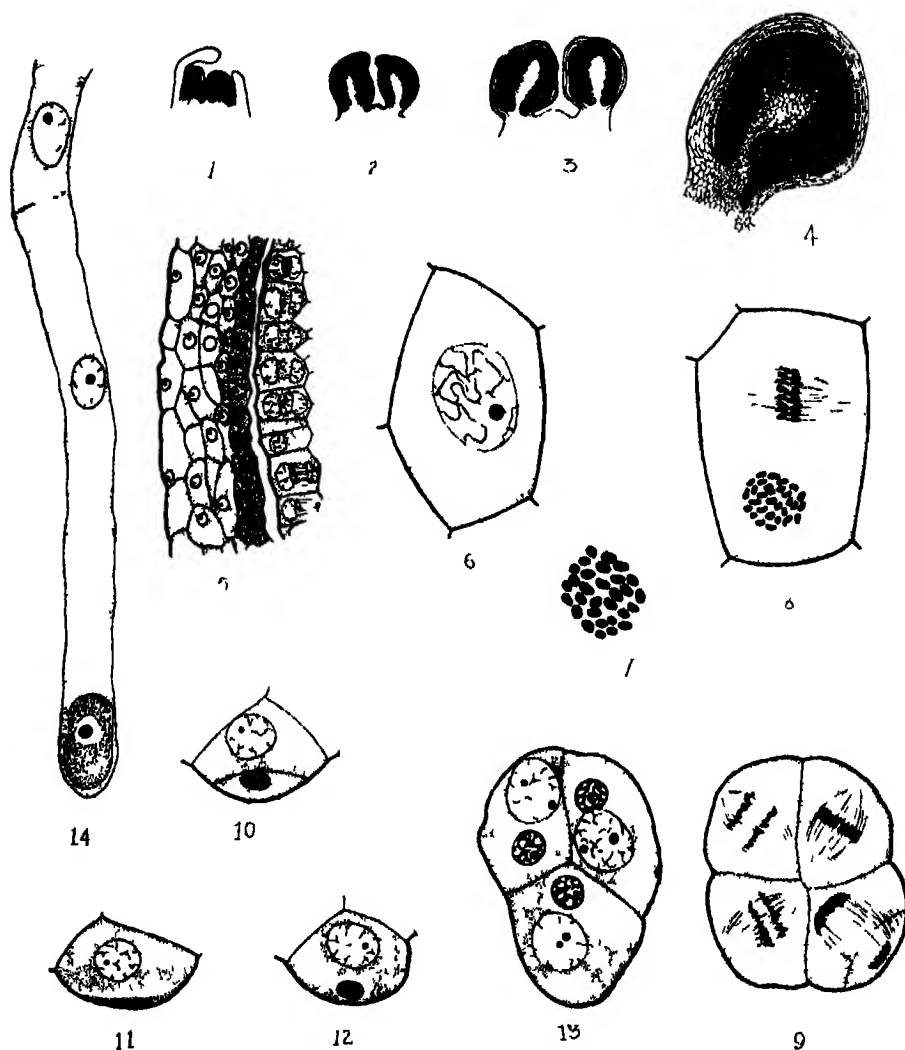
The sepals and petals are free and spreading. The spurred lip is erect and arises from the base of the column, which is up to  $\frac{3}{4}$  inch in length. The sepals, petals and lip are marked with red crested nerves. The anther is two-celled and occupies a terminal position (Figs. 15 and 16). The short-stalked pollinia are attached to the discoid gland in the rostellum.

## Microsporogenesis and male gametophyte

The primordium of the anther originates as two adjacent protuberances (Fig. 1) consisting of actively dividing cells. At an early stage, the central cells become elongated and highly vacuolated, forming a core of sterile cells in the centre. The rest of the cells lying between the core and the epidermis remain highly protoplasmic and form the sporogenous tissue (Figs. 2 to 4).

The parietal tissue in the anther consists of 2 to 3 layers of cells towards the distal and 5 to 6 layers towards the basal end. Some of the tapetal cells divide periclinally so as to form a 2-layered tapetum at places here and there (Fig. 5).

The microspore mother cells (Fig. 6) undergo the usual stages of reduction division. Thirty bivalents were counted in the metaphase plate of the first division (Fig. 7) and the same number of univalents in the second division (Fig. 8). The resulting quartets may be either isobilateral (Fig. 9) or tetrahedral (Fig. 13).



Figs 1 to 4—Diagrams representing the differentiation of the sterile core of cells and the sporogenous mass of the anther,  $\times cu$  267 Fig 5—A portion of the anther showing wall layers, tapetum and dividing microspore mother cells,  $\times 840$  Fig 6—Microspore mother cell,  $\times 1200$  Fig 7—Metaphase plate of division I,  $\times 1200$  Fig. 8—Metaphase of division II,  $\times 1200$  Fig 9—Microspores of an isobilateral quartet dividing,  $\times 1200$  Fig 10—Division of the microspores,  $\times 1200$  Figs 11 and 12—Stages in the movement of the generative cell,  $\times 1200$  Fig 13—A tetrahedral quartet at the time of shedding,  $\times 1200$  Fig 14—Pollen tube with two male nuclei and the degenerating tube nucleus,  $\times 1200$

In the division of the microspore, the generative cell is always cut off towards the exterior (Fig 10) The resulting nuclei and cells are unequal in size almost from the very beginning, the generative cell and nucleus being

smaller than the vegetative but displaying a greater avidity for stains than the latter. After a time the wall between the two cells disappears and its place is taken by a clear space (Fig. 11). The generative cell changes its original shape and becomes spherical, its cytoplasm becoming so hyaline and transparent as to look like a clear space. The plasma of the vegetative cell gradually engulfs the generative and completely surrounds it (Fig. 12). At this stage the position of the engulfed generative cell varies greatly even in the same quartet and gives no indication of the original place where it was cut off (Fig. 13). Pollinia are shed at this two-celled stage of the male gametophyte.

The microspores do not separate even at maturity. Pollen tubes are put forth simultaneously from all the four cells of the quartet. In most cases the tube nucleus is the first to enter the pollen tube but in a few instances the reverse may happen. Eventually the tube nucleus occupies the tip of the tube and becomes slightly hypertrophied before degeneration sets in. The actual division of the generative nucleus was not noticed. The two male nuclei are ovate in shape and lie behind the tube nucleus (Fig. 14).

The pollen tubes pass through the stylar canal along the large vacuolate cells that form the core of the column and reach the ovary about a week after pollination. Within the ovary they proceed along on either side of the three placental ridges (Fig. 17) and then distribute themselves to the ovules. Successful pollination is externally indicated by the enlargement of the gynostegium.

### *Ovule*

The ovule becomes completely anatropous at a very early stage of development. The origin and growth of the integuments can be followed from figs. 18 to 20. The inner coat consists of two layers of cells while the outer is single-layered and remains so till the end. During post-fertilisation stages the inner integument, together with the few nucellar cells at the chalaza, becomes completely disorganised so that the developing embryo is in contact with the outer integument. During later stages (when the proembryonal cells are elongating) the nuclei of the outer integumental cells also disintegrate, their cell walls thicken and become translucent. It may be mentioned here that because of this feature many of the post-fertilisation stages are very suitable for microscopic examination when whole mounts of the ovules are prepared in lactophenol or chloral hydrate.

### *Embryo-sac and Fertilisation*

A single hypodermal archesporial cell differentiates in the nucellus about a week after pollination. No parietal cells are cut off. Usually a T-shaped tetrad of megaspores is formed (Fig. 21), though linear ones are also frequent. The micropylar dyad cell frequently disintegrates without dividing. The nucellar epidermis becomes disorganised at the 2-nucleate stage of the embryo-sac. The subsequent stages in the formation of the embryo-sac are quite

normal In many cases the mature embryo-sac is only 7-nucleate, due to the failure of division of one of the chalazal nuclei at the 4-nucleate stage of the

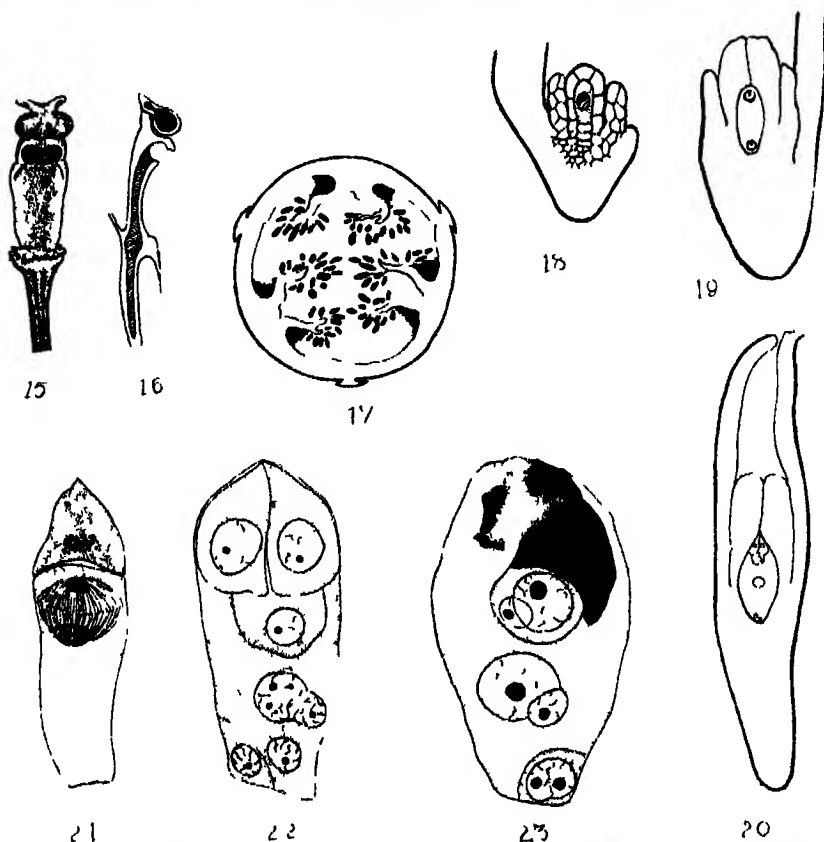


Fig 15—Gynostegium and ovary, perianth removed,  $\times ca 34$  Fig 16—Optical longitudinal section of Fig 15, viewed from the out surface Pollinium is shown as a black mass The stylar and the ovarian cavities are shaded,  $\times ca 34$  Fig 17—Transverse section of the ovary, showing the placental ridges and the pollen tubes on either side of the ridges,  $\times ca 14$  Figs 18 to 20—Stages in the development of the ovule,  $\times ca 267$  Fig 21—A stage in the formation of the megaspore tetrad,  $\times 1200$  Fig 22—Mature embryo sac,  $\times 1200$  Fig 23—Double fertilisation,  $\times 1200$

sac (Fig 22) The egg apparatus is organised as usual at the micropylar end and the polar nuclei fuse just before fertilisation

The pollen tube enters the sac through the micropyle and double fertilisation takes place normally (Fig 23) The primary endosperm nucleus, formed after triple fusion, degenerates without any further development

### *Embryogeny*

The first division of the zygote is transverse The next 3 to 6 divisions are very irregular and take place without any definite sequence, resulting

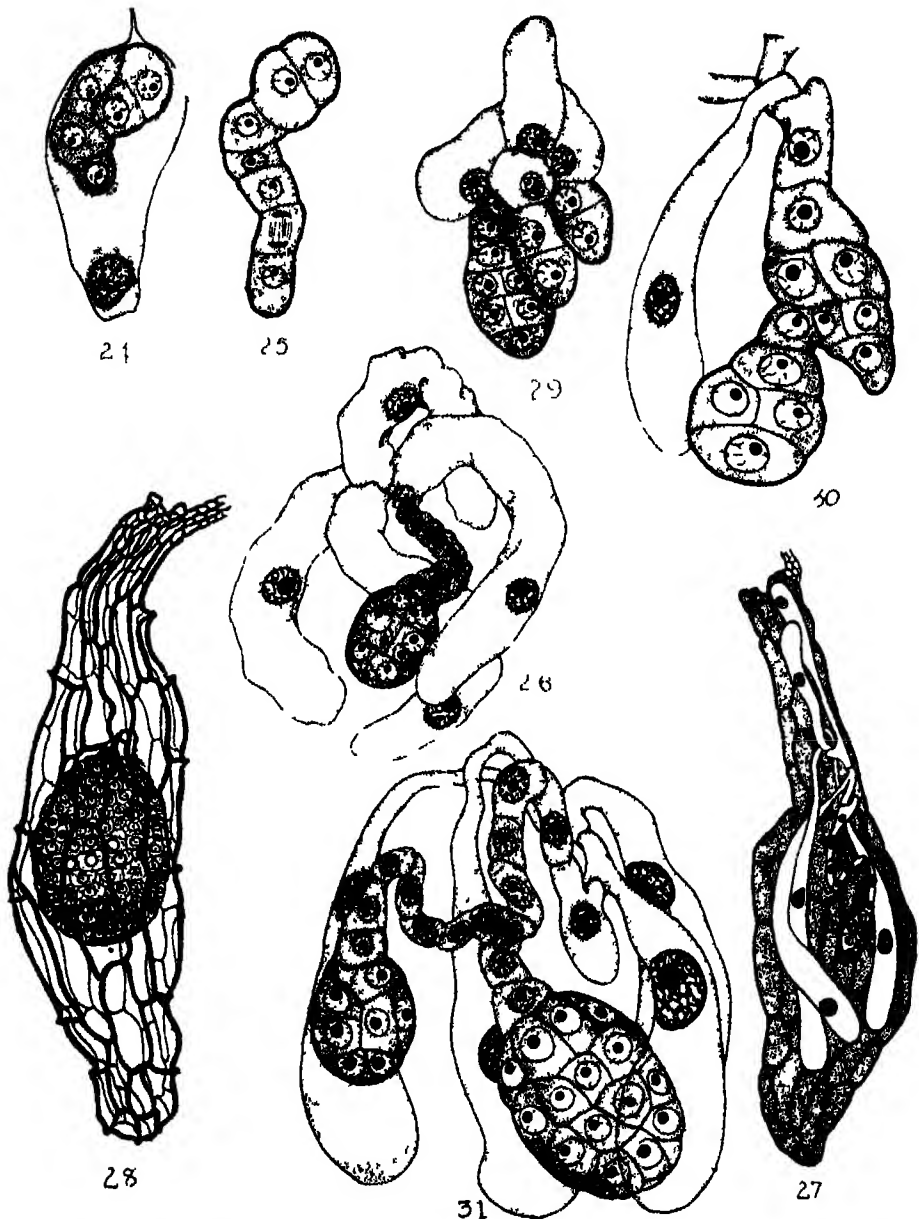


Fig 24—An early stage in the formation of the embryo, showing the irregularly divided mass of cells,  $\times ca. 534$  Fig 25—Formation of the filamentous proembryo,  $\times ca. 534$  Fig 26—A typical stage in the development of the embryo, four of the proembryonal cells have elongated and enlarged,  $\times ca. 534$  Fig 27 - Optical l's of the developing seed showing the relation of the suspensor cells to the surrounding tissues,  $\times ca. 107$ . Fig. 28—Mature seed showing the transparent seed-coat and the embryo inside,  $\times ca. 107$ . Figs 29 to 31—Stages in polyembryony; for explanation see text,  $\times ca. 534$ .

in a mass of irregularly arranged cells (Fig 24) One of the terminal cells of that irregularly arranged mass divides periclinally to form a filamentous row of 7 to 10 cells (Fig 25) On the other hand, the cells at the micropylar end—usually 6 to 8—elongate and protrude (Fig 26) out of the disorganised tissue of the inner integument and come in contact with the cells of the outer integument (Fig 27) Their nuclei get hypertrophied to 5 or 6 times of their original size At the same time 2-3 of the terminal cells of the pro-embryonal filament divide by vertical and oblique walls to give rise to the actual embryonal mass, which occupies a more or less central position in the ovule The elongated cells of the suspensor wither away and become inconspicuous in the mature seed The embryo now lies suspended in the cavity of the seed-coat by the degenerated and shrivelled tissue of the inner integument The fruits open 5 to 6 months after fertilisation

### *Polyembryony*

Additional embryos, which are sometimes present, are formed in one of the following ways —

- (1) The zygote divides irregularly to form a mass of cells, some of which lying at the chalazal end develop simultaneously and give rise to multiple embryos (Fig 29)
- (2) The filamentous proembryo becomes branched and an embryo may be formed at the tip of each branch as shown in fig 31 In one case as many as three embryos were found to have arisen in this fashion
- (3) Buds are given out from the embryo itself and these produce additional embryos (Fig 30)

### *Conclusion and Summary*

Certain stages in the development of the male gametophyte show a close resemblance with those in *Cymbidium bicolor* Lindl (Swamy, 1941) The most important features of resemblance are the remaining together of the microspores of the quartet, the cutting off of the generative cell towards the exterior and its later passage into the vegetative cytoplasm, and the division of the generative nucleus into two sperm nuclei in the pollen tube

In the development of the embryo-sac there is a reduction in the number of antipodal nuclei, a feature which is not uncommon in the Orchidaceae (see Schnarf, 1931, p 276) Recently it has also been reported in *Acroanthus* (Stenar, 1937-38) and *Cymbidium* (Swamy, 1942) Sharp (1912) regards this as a tendency towards the reduction of the vegetative portion of the gametophyte

Except for some minor variations the course of development of the embryo also resembles that of *Cymbidium bicolor* (Swamy, 1942) The filamentous region of the proembryo is curved in the form of a sigma consisting of 10-15 cells In *Cymbidium*, on the other hand, it is composed of only 5 to 10

cells becoming crushed in later stages between the embryonal mass and the prolongations of the suspensor cells

Polyembryony originating by budding or proliferation of the sexually produced embryo or proembryo or zygote is termed cleavage polyembryony. This is admittedly a rare phenomenon in Angiosperms. In a previous paper the writer (Swamy, 1942) recorded its occurrence in *Cymbidium bicolor*, the only other form previously recorded for Orchidaceae being *Limnorchis*<sup>1</sup> (Ernst, 1918). *Eulophea epidendraea* is another instance of this type of development.

The author wishes to take this opportunity to express his deep sense of gratitude to Dr P Maheshwari of the Dacca University for his able criticism and guidance throughout this investigation.

### POSTSCRIPT

Since forwarding this paper to the press, A Ernst's monograph, 'Bastardierung als Ursache der Apogamie im Pflanzenreich (1918)', was available for reference to the author. In it no reference of any sort is made to *Limnorchis* by Ernst. It is quite probable that Webber has overlooked this fact or the original was not accessible to him. In view of these, the present case will have to be considered as the second instance among orchids to exhibit the cleavage type of polyembryony, the first being *Cymbidium bicolor* Lindl (Swamy, 1942).

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<sup>1</sup> The original paper was not available for reference. The literature has been cited from Webber [*Bot Rev.*, 6, p 578 (1940)] where the plant referred to is printed as *Limnorchis* (Orchidaceae). Since no genus by this name occurs in Orchidaceae, it might probably be *Limnorchis*.



# PHOTO-CHEMICAL ANALYSIS

## PART II

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(Communicated by Dr N R Dhar, DSc, FNI, IES)

(Received November 9, 1942.)

In a previous communication Gopala Rao and Ramacharlu (1942) have reported the development of a new technique for quantitative chemical analysis. The photo-chemical reaction between mercuric chloride and sodium oxalate has been employed as the basis of a method for the quantitative estimation of mercuric chloride. This reaction takes place rather slowly when the reaction mixture is exposed to sunlight in glass vessels, hence they employed uranyl nitrate as a photo-sensitiser to accelerate the reaction. In this way, the reduction of the mercuric chloride to mercurous chloride can be made to occur quantitatively in sunlight or in the light of the quartz mercury vapour lamp under conditions specified in the paper. It was, however, noticed that with uranyl nitrate as photo-sensitiser the reaction does not take place rapidly enough in the light from a 1,000 watt tungsten filament lamp. Many laboratories may not afford an ultraviolet ray equipment, moreover, uranium salts are costly. We, therefore, attempted to use a cheaper photo-sensitiser which will permit exposures from a 1,000 watt tungsten filament lamp. We found that ferric chloride answers the purpose at very low concentrations. In this paper we describe the conditions under which a quantitative reduction of mercuric chloride by oxalate can be effected with ferric chloride as photo-sensitiser with different types of illumination.

### EXPERIMENTAL

A mixture of the requisite quantities of mercuric chloride, sodium oxalate, and the photo-sensitiser was exposed to light and after the reaction was over the mixture was treated with an excess of a solution of iodine in potassium iodide as in the previous work. The iodine reacted with the precipitated mercurous chloride, and the unreacted iodine was titrated with a solution of standard sodium thiosulphate. From the amount of iodine consumed one could calculate the amount of mercuric chloride originally taken.

From a large number of trials it was found that the use of ferric chloride at high concentrations results in the further reduction of mercurous chloride to metallic mercury even in short exposures. A solution of M/100 ferric chloride in M/100 hydrochloric acid was prepared and preserved in a stoppered brown

**Jena bottle** The presence of hydrochloric acid and the mode of preservation prevented the hydrolysis of ferric chloride for a considerable time. From this stock solution was prepared by dilution with distilled water the M/10,000 solution of ferric chloride just before it was required for use as photo-sensitiser. Otherwise solutions of this dilution undergo marked hydrolysis very rapidly. It was noticed by us that solutions containing hydrolysed ferric chloride do not exhibit marked photo-sensitisation. It must also be remembered that the concentration of hydrochloric acid cannot be kept too high because the reduction of mercuric chloride is inhibited by a high hydrogen ion concentration. A few typical results from out of the many obtained in sunlight are given in the table below.

TABLE I

X ml of M/20  $\text{HgCl}_2$  + X ml of N/5  $\text{Na}_2\text{C}_2\text{O}_4$  + X/5 ml of M/10,000  $\text{FeCl}_3$  exposed for one hour to sunlight in 100 ml Monax conical flasks

Milliliters of $\text{HgCl}_2$ solution taken	Milligrams of mercury taken	Milligrams of mercury found
1	10.03	10.11
2	20.06	20.05
5	50.15	50.15
7	70.21	70.21
10	100.30	100.2
15	150.45	149.9

Ferric chloride at this dilution does not liberate iodine from potassium iodide in amounts detectable even by starch. Hence its presence will not vitiate the iodometric estimation of mercurous chloride.

*Experiments in the light of a quartz mercury vapour lamp*

The mixture of mercuric chloride, sodium oxalate and ferric chloride was exposed in a conical flask kept underneath the arc. It was found necessary to employ a higher concentration of ferric chloride, namely M/3,000.

TABLE II

X ml of M/20  $\text{HgCl}_2$  + X ml of N/5  $\text{Na}_2\text{C}_2\text{O}_4$  + X/5 ml of M/3,000  $\text{FeCl}_3$  exposed for one hour

Milliliters of $\text{HgCl}_2$ solution taken	Milligrams of mercury taken	Milligrams of mercury found
1	10.03	10.04
2	20.06	20.08
5	50.15	50.12
7	70.21	70.16
10	100.30	100.1

The mercury arc was of the Hereaus type worked on 220 volts D.C. at 3.5 amps.

*Experiments in the light from a 1,000 watt tungsten filament lamp*

The mixture was exposed in a 100 ml conical flask kept underneath the electric bulb. The lamp was worked on the 220 volts A C mains at 4 amps. It was found necessary to use a high concentration of ferric chloride of the order of M/50. Ferric chloride at this concentration liberates iodine from potassium iodide, but in the presence of excess of oxalate it does not do so. Hence, even this high concentration of ferric chloride will not interfere with the iodometric estimation under these conditions.

TABLE III

X ml of M/20  $\text{HgCl}_2$  + X ml of N/5  $\text{Na}_2\text{C}_2\text{O}_4$  + X/5 ml of M/50  $\text{FeCl}_3$   
exposed for two hours

Milliliters of $\text{HgCl}_2$ solution taken	Milligrams of Hg taken	Milligrams of Hg found
1	10.03	10.05
2	20.06	20.12
5	50.15	50.22
7	70.21	70.04

We also found that much smaller quantities of mercury can be estimated than those indicated in the tables. We refrain from giving the results for lack of space.

## SUMMARY

1 From the results presented in this paper it is evident that ferric chloride, at suitable concentrations, serves as a good photo-sensitiser for the quantitative reduction of mercuric chloride by oxalate in sunlight. Moreover, the use of ferric chloride enables us to work with a cheap source of artificial light, namely, a 1,000 watt tungsten filament lamp.

2 Our experiments showed further that with ferric chloride as photo-sensitiser one can carry out the reaction in sunlight in brown glass bottles. With brown glass bottles the danger of reduction of mercurous chloride to metallic mercury due to unduly long exposures is entirely eliminated. Under these conditions one can also use with safety higher concentrations of ferric chloride than have been indicated in Table I.

We desire to express our grateful thanks to Prof N R Dhar, D Sc. (Lond.), Dr ès Sciences (Paris), F I C, I E S, of Allahabad for his interest in this work. One of us (P T R) is indebted to the authorities of the Andhra University for the award of the Kistna District Board Research Fellowship.

## REFERENCE

Gopala Rao, G and Ramacharlu, P T, (1942) Photo-chemical Analysis Part I  
*Proc. Nat Inst Sci Ind*, 8, 383-388



## SYMPOSIUM ON 'HEAVY CHEMICAL INDUSTRIES IN INDIA'

### INTRODUCTORY NOTE

At the meeting of the Council of the National Institute of Sciences of India held on the 4th February, 1941, it was suggested to hold a Symposium on 'Heavy Chemical Industries in India' at either Bangalore or Delhi. After consulting the Members of Council residing at these two places it was finally decided to hold the Symposium at the Ordinary General Meeting of the Institute to be held at Delhi by the middle of April, 1941. Sir S. S. Bhatnagar and Dr. (now Sir) J. C. Ghosh were requested to organise the Symposium. The Symposium was held at the Physics Lecture Theatre of the University of Delhi on the 19th April, 1941.

Owing to preoccupations of possible contributors and shortness of notice it was not possible to secure a sufficient number of contributions which would correctly reflect the present position of heavy chemical industries in India and the present and future problems of developing them. A considerable number of important contributions representing various aspects of the subject were, however, received and they are published in the following pages. Naturally, attention has been pointedly drawn by several speakers to the manufacture of sulphuric acid, the position regarding which requires close examination and watch. The contributions deal with phosphatic fertilisers, cyanamide, urea and allied substances, glycerine, magnesium chloride, potash salts, water glass, acetic acid and formaldehyde. The manufacture of these substances, which are of great importance for a number of our basic industries, has acquired special importance at the present moment.

The war has drawn attention to a group of correlated factors which, although of fundamental importance in the industrial development of a country, have not hitherto been much noticed in India. The most important among these are a planned and systematic survey of the available basic raw materials including minerals and forest products, and the development of industries for processing them to the finished goods stage instead of exporting them in the 'raw' condition and importing the finished products. Other questions of fundamental importance are the co-ordinated development of the transport system of the country, prosecution of fundamental and applied research in the Universities and technological institutions and the training of skilled labour. The Symposium draws attention to some of these problems and shows the attempts which are being made by official and non-official agencies to tackle them.—S. P. AGHARKAR, *Honorary Secretary*



# UTILISATION OF THE STRONTIUM MINERALS OCCURRING IN TRICHINOPOLY DISTRICT, MADRAS

*By N JAYARAMAN, Indian Institute of Science, Bangalore*

*(Read at Symposium, April 19, 1941)*

Almost all the workable strontium deposits of the world are of sedimentary origin. Generally strontium occurs as the sulphate, celestite and the carbonate strontianite. Even though both these minerals of strontium are rare, celestite seems to be more common than strontianite. Its presence in minute traces in surface waters is also recognised. It is present in large quantities in some springs and well waters. The manner in which the minerals celestite and strontianite occur in sedimentary rocks varies widely. In many cases the crystals of these minerals occur throughout the sedimentary rock formations of a particular area. They also occur as large lumps and as continuous rock masses interstratified with other formations. Sometimes these occur as fairly good crystalline aggregates on the surface of eroded sedimentary rocks along with gypsum.

Strontium either as celestite or as strontianite occurs in all the countries of the world. But its occurrence is rather limited. Only a few countries possess large deposits of these minerals. Some of the larger deposits occur in places which are very inaccessible and so they are not being worked at present.

Till recently it was considered that the occurrence of strontium was rare in India. In 1939 the author of this paper discovered the presence of a large deposit of strontium minerals in the cretaceous rocks of Trichy District. Before the discovery of this deposit, there were only three recorded occurrences of strontium minerals in India. Blanford of the Geological Survey of India, in one of his memoirs, refers to an occurrence of strontium as having been found by Fedden in Western Sind. It is reported that it occurs only very sparingly and as scattered crystalline lumps on the surface of the Kirthar limestone hills of Kohistan. The occurrence of a small quantity of strontium minerals was also found by A. B. Wynne in red clays of Tertiary age in Kohat District, N.-W. Frontier Province. Jones reports the occurrence of small quantities of strontium sulphate along with large quantities of barium sulphate in the nodules dredged off Colombo. The occurrences mentioned above are very limited and so no economic exploitation of these deposits was attempted. At present almost all the strontium consumed by India is imported, but statistics are not available to find out the quantities involved.

While engaged in a mineralogical and chemical study of the phosphatic nodules from Trichinopoly, the author noticed the presence of a crystalline white mineral which filled up the septarian cracks in the nodules. This mineral was also found to occur as fan-like radiating aggregates even in nodules which were free from the septarian cracks. On examination it was identified to be celestite. On the average, the phosphatic nodules hold about 3% celestite and in some cases it is as high as 15%. Previous investigators of the phosphatic nodules had mistaken this mineral for gypsum which is also found along with celestite. The presence of celestite in the phosphatic nodules led the author to look for its occurrence outside the nodule also, viz., in the clay beds in association with gypsum. A trip to the area was arranged and a detailed examination of the clay beds N-E of Utatur, a village situated about 20 miles to the N-E of Trichy, revealed the presence of large quantities of celestite.

The mineral celestite occurs here along with gypsum as lumps of varying sizes. Masses weighing from 50 to 60 lbs are also met with. A block of celestite weighing about 75 lbs has been kept at the Indian Institute of Science Museum for exhibition. These masses are invariably made up of radiating and parallelly arranged columnar crystals of celestite. The individual columnar crystal of such masses has a maximum thickness of about 0.5 cm and a maximum length of about 7 cm. Unaltered and washed specimens give on analysis about 95%  $\text{SrSO}_4$ . But most of these lumps of celestite were found to be in varying stages of alteration, the main product of alteration being a fibrous strontianite. In many places the original celestite blocks have been completely altered to strontianite and in some they have given place to a yellow amorphous earthy material. This material was also found to be composed mainly of strontium carbonate with a large admixture of silica and other impurities. The celestite and its alteration products are found occurring in small isolated heaps over a large area covering sixteen to twenty square miles. Their occurrence is rather abundant in an area of nearly 2,000 acres adjoining Karai and Thirani villages. On a rough preliminary survey, it is estimated that this deposit contains about a million tons of celestite and some strontianite. On the average these minerals contain about 45% strontium oxide which is equivalent to nearly 80%  $\text{SrSO}_4$ . Researches carried out at the Indian Institute of Science by the author indicate that it is possible to treat the powdered strontium minerals from Trichy with a view to remove most of the objectionable impurities such as silica, clay, calcium phosphate and calcium carbonate, by cheap physico-chemical processes and obtain a concentrate containing over 96% strontium sulphate.

Though the area in which the celestite and strontianite occur was surveyed so long ago as 1865 by the Geological Survey of India, the presence of these minerals was not even suspected (except in one case where a photograph of a lump of celestite has been published by Ramaswami Sivan in some other connection) in these areas, the deposits being generally mistaken for gypsum.

which also occurs in this locality in considerable quantities. The gypsum is for the past few years being worked by some private companies which have been assigned the lease of this area only for the mining and exploitation of gypsum. In the course of a survey of this area in December 1939 the author found that these companies, being ignorant of the identity of the celestite and strontianite found in large quantities amidst the gypsum, had as a rule collected them in dumps as of no value, while a percentage of these minerals was also being mixed up by inadvertence with the gypsum that was mined and removed, because of the inability of the pickers employed by these companies to distinguish in all cases between gypsum on the one hand and the other two aforementioned minerals on the other. But now, after the discovery of the strontium minerals was announced, some of these companies have applied for and obtained mining rights for these minerals also.

Detailed investigations carried out by the author at the Indian Institute of Science showed that the finely powdered celestite from Trichy is easily decomposed by heating it in a 10% solution of ammonium carbonate. Complete decomposition was effected after heating the solution for two hours. The resulting solution contained most of the strontium as strontium carbonate precipitate and all the sulphur as ammonium sulphate in solution. Thus, most of the ammonia used as ammonium carbonate could be recovered as ammonium sulphate which could be considered as a valuable by-product. The strontium carbonate is the most important compound of strontium so far as its industrial utilisation is concerned. Because, it is the starting material for the preparation of the other compounds of strontium. The strontium oxide, which is extensively employed for the manufacture of beet sugar and for the complete extraction of sugar from cane molasses, is prepared from strontium carbonate by heating the latter in the presence of steam and coal. Strontium oxide is also prepared by igniting the nitrate, but this process is not practised for the large-scale production of the oxide. Strontium hydroxide, obtained by adding water to the oxide, is the material which is actually employed in the sugar industry. The sugar combines with the strontium hydroxide to form strontium saccharate, which being difficultly soluble separates out. This is then filtered out and treated with carbon dioxide, when strontium is deposited as carbonate. The sugar in the solution is recovered by filtering off the solution, evaporating it and then treating it in a refinery. The other use for strontium salts (especially strontium nitrate) is for the production of red light of fireworks. Strontium salts are also used in medicine.

America and other countries, which produce beet sugar on a large scale, are big consumers of these strontium minerals as they are essential for the production of this kind of sugar. Especially in America the demand for strontium salts is very great. As India is not a big consumer of strontium salts most of the strontium, either in the state of concentrated celestine powder or as manufactured strontium carbonate could be exported at a great profit.

The latter process is more advantageous since the by-product (ammonium sulphate) resulting from this process is a valuable fertiliser

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The author of this paper has also worked out a process for the preparation of strontium carbonate from the Trichy celestite using soda ash. This process has been handed over to a company at Trichy which would shortly start producing strontium carbonate. The author of this paper has also worked out processes for the manufacture of the other compounds of strontium, viz chloride, nitrate and the hydroxide, from the Trichy celestite.

# MANUFACTURE OF UREA, DICYANDIAMIDE, MELAMINE, GUANIDINE CARBONATE AND GUANYL UREA SULPHATE

*By Y SANKARANARAYANAN and H K SEN, Indian Lac Research Institute,  
Namkum, Ranchi*

*(Read at Symposium, April 19, 1941)*

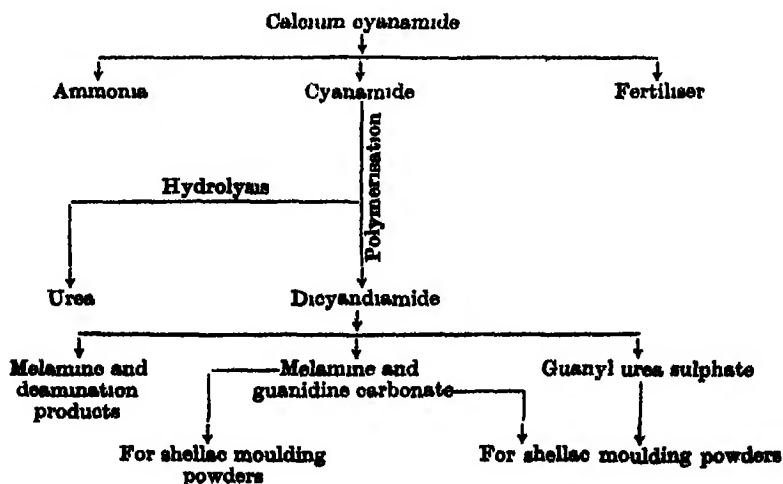
Aminoplastics form one of the main branches of the synthetic plastic industry of modern times. That urea and formaldehyde condense to produce resins when treated under suitable conditions was observed as early as 1884, and since then a great many varieties of urea formaldehyde resins have been prepared suitable for different purposes. In addition to its use as a starting material for synthetic resins, urea finds other wide applications as a fertiliser and in medicine for the preparation of certain specifics like urea-stibamine, etc. The immediate interest that drew the attention of the Indian Lac Research Institute to the production of this chemical on a large scale was created by the fact that shellac when suitably compounded with urea and formaldehyde gives rise to a resin which with proper fillers yields moulding powders which could be used for producing articles in the compression moulding press, working on the Bakelite technique. This powder has been found to be a cheap and suitable substitute for the now very familiar bakelite. In addition to urea, several other related nitrogenous substances like cyanamide, dicyandiamide, and guanidine are known to be usable for the production of synthetic resins. The latest addition to this list is melamine, the resins from which have been found to have very remarkable properties as regards hardness, transparency and heat and water resistance. It finds extensive application in the textile field where fabrics are rendered antireseal with the aid of a melamine formaldehyde resin. It is also known for the readiness with which it forms resins with sugars, phenols, aniline, etc., thereby resulting in a very wide range of products useful for a variety of purposes. Melamine also, like urea and the other chemicals mentioned above, has been found to be useful for the production of shellac moulding powders. Attention was therefore directed to evolve suitable methods for the production of these chemicals on a large scale using, as far as possible, only such raw materials as are readily available or produced in India, in plants that could be made in the country. It is hoped that the manufacture of these chemicals cheaply and in sufficient quantities will not only lead to the establishment of a sound shellac moulding powder industry but also give a great filip to the starting of urea and melamine resins in this country.

*Urea*

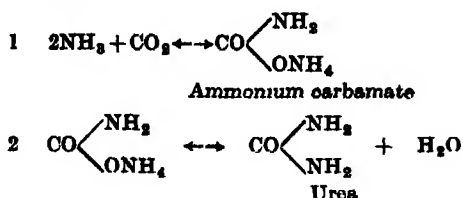
There are several processes known for the production of urea but only two of these are being exploited commercially. The main raw materials are ammonia and carbon dioxide in the one and calcium cyanamide in the other.

Carbon dioxide and ammonia are available even under present circumstances, and their availability could be considerably increased by properly organising the existing coke oven and fermentation industries. Besides, limestone being plentiful, a gaseous mixture containing about 30%  $\text{CO}_2$  may be readily obtained by burning a 7 : 1 mixture of limestone and coke, the lime obtained thereby being used for the generation of ammonia from ammonium sulphate. Another alternative method would be the burning of coke with a minimum excess of air. The carbon dioxide thus obtained may be passed into potassium carbonate solution to produce potassium bicarbonate, which, on heating, liberates pure carbon dioxide, leaving the carbonate ready again to absorb fresh carbon dioxide.

Calcium cyanamide, the alternative starting material for the manufacture of urea, is itself a fertiliser, and is produced in large quantities in Europe and America. It used to be imported in good quantities before the present war, and is even now available in India in moderate lots. But the establishment of a calcium cyanamide plant in this country is by no means difficult and with the rapid development of our hydroelectric schemes, the day may not be far off when a thriving calcium cyanamide factory makes its appearance. The rise of such an industry will naturally lead to cheaper ammonia, thereby making the entire process more profitable. The utility of calcium cyanamide in the manufacture of certain nitrogenous heavy chemicals will be seen from the scheme below —



The main reactions in the formation of urea from carbon dioxide and ammonia are as follows —



The first reaction takes place when *dry* ammonia and carbon dioxide (in the volume ratio of 2 : 1) are passed into a cooled chamber. The ammonia may be dried by passing it through suitable towers filled with lumps of quicklime and the carbon dioxide dried by passing it through a sulphuric acid scrubber. The dry gases in the proper proportion are allowed to mix in a sufficiently large chamber where they combine to form ammonium carbamate with evolution of heat. As the carbamate dissociates even at lower temperatures, the chamber is maintained cold artificially by an external spray of cold water. The temperature is maintained at about 25°C and on no account should be allowed to rise beyond 30°C. As the reaction is a reversible one, the gases issuing from the reaction chamber, A, always contain the unreacted ammonia and carbon dioxide which can be recovered by passing the mixture through vessels C, C, containing a fine suspension of gypsum in water. Here the ammonia and carbon dioxide get fixed as ammonium sulphate and calcium carbonate respectively. This ammonium sulphate is recovered and re-used for the generation of ammonia. On opening the carbamate chamber, B, plenty of ammonia is evolved and this also may be recovered as stated above.

The collection of ammonium carbamate from the sides of the carbamate plant is rather difficult, as the carbamate forms a rather hard incrustation. Therefore, the plant must be provided with a very efficient scraping equipment as shown in the figure 1.

The next stage is the conversion of ammonium carbamate into urea. This conversion does not usually exceed 43% of the theory, working under the best of conditions (170°–180°C for six hours). But by conducting the reaction in the presence of a large excess of ammonia the yield of urea may be raised to as high as 80% of the theory, by using both ammonia and carbon dioxide under pressure. The carbamate is packed inside the autoclave of appropriate thickness, the packing ratio being not less than 0.7 gm. (preferably 1 gm.) per cc volume of the bomb. The heating may be conducted by gas or electricity and the contents of the autoclave are maintained at about 180°C for six hours. The pressure registered is about 1,500–1,800 lbs. per sq. inch. As stated before, the conversion proceeds only to the extent of 40–43%, the rest remaining as carbamate and a part hydrolysed as ammonium carbonate. After cooling, the autoclave is opened and the issuing gases (ammonia and carbon dioxide) recovered in the gypsum tower as stated above. Water is

then poured in and the urea dissolved out. The concentrated solution is filtered off from suspended impurities if any and then evaporated till a few c c taken on a metal surface solidifies almost immediately. The unreacted carbamate and the carbonate formed decompose during concentration and the gases are recovered as described earlier. The practically fused urea is then poured out into a quadrangular dish of steel or copper lined inside with tin and allowed to set. The urea is pure enough to be directly used for most purposes

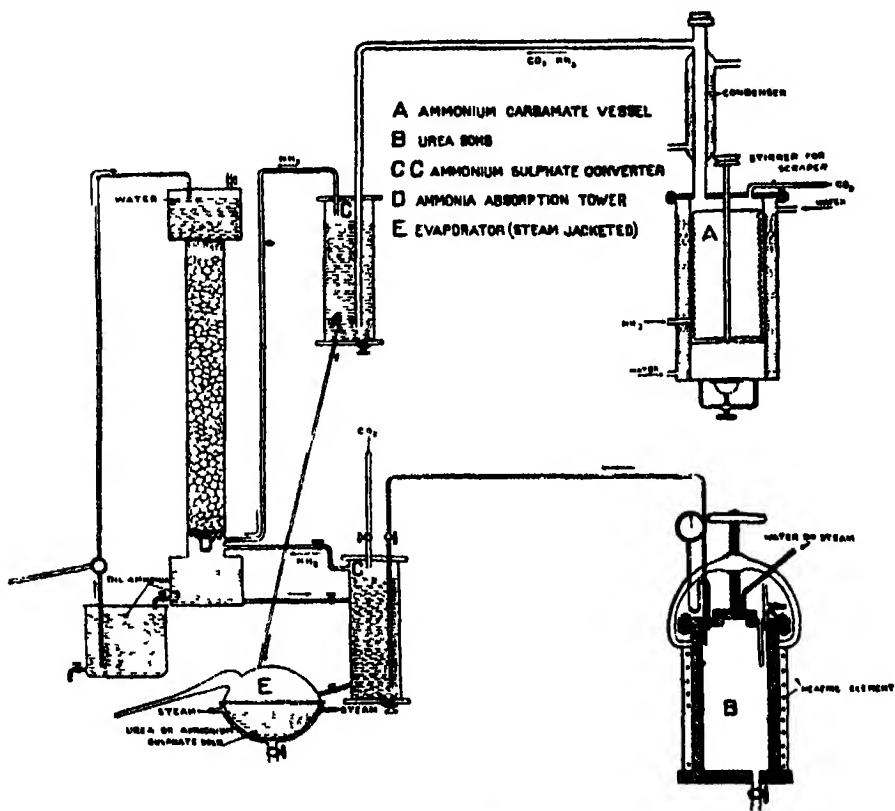


FIG. 1 Urea Plant

*Cost sheet*

		Rs.
<b>A Capital Expenditure—</b>		
4 Urea bombs (1½' diam. × 3' height)		2,800
<b>Carbamate Plant—</b>		
Ammonia generator		200
3 Condensation chambers (3' diam × 8' height)		2,250
3 Ammonia drying towers		300
4 Absorption towers		400
Evaporating pan (steam jacketted)		1,000
Small steam boiler		3,000
Lime-kiln		500
Gas holder 1,000 c ft		1,500
Compressor		1,500
Cylinder for compressed CO <sub>2</sub>		150
Filter press		400
Vats, etc		200
Mounting (including pipe lines, etc )		500
Building		2,000
	<b>TOTAL</b>	<b>16,700</b>
<b>B Process charges—</b>		<b>Rs    A    P</b>
Depreciation at 10% on block account		5   10   0
Interest at 5% on block account		2   13   0
Supervision		5   0   0
Labour		3   0   0
	<b>TOTAL</b>	<b>16   7   0</b>
<b>C Cost of materials—</b>		
Ammonium sulphate 1,056 lbs , @ Rs 190 per ton		89   8   0
Lime 448 lbs , @ Re 1 per cwt		4   0   0
		<b>93   8   0</b>
Less cost of 1,088 lbs CaSO <sub>4</sub> produced in the reaction, @ Rs 20 per ton		9   12   0
		<b>83   12   0</b>
Plus 5% for unpurities cost of 272 lbs of dry ammonia		4   4   0
		<b>88   0   0</b>
1,600 lbs limestone, @ Rs 10 per ton		7   0   0
800 lbs coal equivalent to all charges of heating, compression, scrubbing, etc , @ Rs 10 per ton		3   8   0
		<b>10   8   0</b>
Less 896 lbs lime, @ Re 1 per cwt		8   0   0
		<b>2   8   0</b>
Cost of 352 lbs. CO <sub>2</sub>		<b>88   0   0</b>
272 lbs. of dry ammonia		2   8   0
352 lbs of CO <sub>2</sub>		<b>90   8   0</b>
Plus cost of 6 cwt. CaSO <sub>4</sub>		8   0   0
Process charges		16   7   0
		<b>112   15   0</b>
Less price of 5.5 cwt of ammonium sulphate		52   4   0
		<b>60   11   0</b>
Less price of 4.25 cwt. of CaCO <sub>3</sub> , @ As.8 per cwt		2   2   0
Cost of 192 lbs urea or cost per lb of urea is about 5 annas		58   9   0

For very large-scale operations, liquid ammonia and liquid carbon dioxide are introduced into a pressure and heat resistant bomb where the formation of carbamate and its conversion into urea take place simultaneously. The capital investments on such a plant are naturally considerably more.

### *Urea from calcium cyanamide*

Calcium cyanamide is the other source for the manufacture of limited quantities of urea. Though the price of urea from imported calcium cyanamide is likely to be somewhat higher than when prepared by the above process, the fact that the operation is very much simpler and involves the outlay of only a comparatively smaller capital makes the process attractive for the small-scale producer. The process as worked out at the Indian Lac Research Institute is described below.

Commercial calcium cyanamide (100 lbs) is mechanically stirred in a large lead-lined wooden vat with 50 gallons of water (temperature 30°–35°C) and the aqueous extract is then filtered through a filter-press. The filter-cake is again washed with about 10 gallons of water. The collected filtrate is then treated with dilute sulphuric acid (35 lbs of acid of sp gr 1.84 diluted with 1 gallon of water) till faintly acidic. The precipitated calcium sulphate is filtered off and to the clear filtrate is again added 10 lbs of concentrated sulphuric acid. The solution is then heated in a lead-lined autoclave at 70°C for six hours in an atmosphere of an inert gas under a pressure of 5 atmospheres.\* After cooling, the excess of sulphuric acid is neutralised with calcium carbonate, the solution filtered and the filtrate evaporated till it registers a temperature of 107°C. At this stage, all the iron and most of the calcium sulphate precipitate out. The filtered solution is re-evaporated to 115°C, when, on cooling, urea, pure enough for most purposes, separates out. The mother liquor on reconcentration to 115°C deposits a second crop of crystals. The syrupy mother liquor left over can be used for making shellac moulding powder in place of urea.

### *Cost sheet*

	Rs	A.	P
Calcium cyanamide 100 lbs, @ Rs 9 8-0 per cwt	8	8	0
Sulphuric acid conc 40 lbs, @ 1 anna per lb	2	8	0
Calcium carbonate 12 lbs., @ 1 anna per lb	0	12	0
Cost of labour, supervision, depreciation, etc	6	0	0
Cost of 25 lbs. urea	17	12	0
or 1 lb. of urea will cost approximately 11 5 annas			

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\* The hydrolysis may also be carried out at the ordinary pressure under the same conditions of temperature and time. The yield of urea in this case is of the order of 20–25 lbs from 100 lbs of calcium cyanamide as against 25–30 lbs when the hydrolysis is carried out under pressure as described above.

*Melamine from calcium cyanamide***Dicyandiamide**

Calcium cyanamide (10 lbs) is stirred well with water (5 gallons) at 45–50°C for half an hour. It is then filtered and the residue washed with a further 1 gallon of water. The total volume of the filtrate is noted. Sulphuric acid (sp gr 1.7) is prepared by mixing concentrated acid (sp gr 1.84) and water in the ratio of 8 : 1. The total volume of this acid required to neutralise the whole of the filtrate was determined by titrating a known volume of the latter against a suitably diluted portion of the former (40 to 1,000 c.c.). The filtrate is then treated with exactly half this volume of acid and the temperature then rapidly raised to 80°. At this stage the rest of the acid is added drop by drop in the course of 1½ to 2 hours with constant stirring. The calcium sulphate precipitated is then filtered off and the solution evaporated to crystallisation. The dicyandiamide separates on standing in the form of long needles, M.P. 210°C. The yield is 12 to 13% of the theory. The mother liquor contains some more dicyandiamide together with smaller quantities of urea, melamine, etc. which may be recovered.

Dicyandiamide (600 gms) is mixed with 125 c.c. of ammonia (sp gr 0.90) in a tin-lined steel autoclave and the mixture heated under pressure to 140°C. At this temperature, the highly exothermic reaction begins and the temperature rapidly rises to 160°C. and the pressure to about 700 lbs per sq inch. The mass is maintained at 150° to 160°C for about 1½ hours. After cooling, the bomb is opened and the issuing ammonia recovered.

The sludge in the autoclave is then removed and digested with cold water (2,000 c.c. in 3 lots). After filtration, the filtrate which contains guanidine carbonate is concentrated till a drop on a glass slide immediately deposits crystals. After cooling, the crystals are collected on a filter, washed with a small quantity of water and dried. The yield of guanidine carbonate varies from 150 to 180 gms.

The residue is boiled with enough water, filtered off from the insoluble matters and the filtrate allowed to stand. Beautiful shining plates of melamine separate out on standing, M.P. 350°C. Yield 160–180 gms.

*Cost sheet.*

	Rs. A. P.
Calcium cyanamide 100 lbs	8 8 0
Sulphuric acid 32 lbs	2 0 0
	<hr/> 10 8 0
Less cost of 44 lbs. of calcium sulphate, @ Rs 3 per cwt	1 3 0
Cost of 12½ lbs. dicyandiamide	9 5 0
i.e. the cost per lb. is about 12 annas	<hr/> <hr/>

	Rs	A	P
Dicyandiamide 10 lbs , @ As 12	7	8	0
Ammonia 12 lbs , @ As 5	3	12	0
	11	4	0
Less cost of 3 lbs guanidine obtained as by product	3	0	0
	8	4	0
Process charges	1	8	0
	9	12	0
Cost of 3 lbs melamine or Rs 3 4-0 per lb			

By treating the dicyandiamide in dry alcohol with gaseous ammonia under 3 atmospheres pressure and heating as described above the yield of melamine has been raised to 450 to 480 gms resulting in a very much lower cost of production.

#### *Guanyl urea sulphate*

Dicyandiamide is dissolved in a slight excess of 2N sulphuric acid by heating to about 80°C when the exothermic reaction begins and the temperature rises rapidly to 100°C It is then maintained at this temperature for 1 hour and then filtered and the filtrate allowed to stand overnight The guanyl urea sulphate separates out in the form of tiny crystals The yield is practically quantitative and the mother liquor from one charge may be used for the next one

#### *Cost sheet*

	Rs	A	P
Dicyandiamide 10 lbs , @ 12 annas per lb	7	8	0
Sulphuric acid (1 80) 6 25 lbs , @ 1 anna per lb.	0	6	3
Processing charges	1	12	0
Total cost of 15 lbs. of guanyl urea sulphate	9	10	3
Cost per lb = As 10 25			

## SOME ASPECTS OF THE HEAVY CHEMICAL INDUSTRY IN INDIA

*By S G SASTRY, Mysore*

*(Read at Symposium, April 19, 1941)*

Chemical industries are generally grouped under two main headings —

- (a) Heavy chemical industries
- (b) Fine chemical industries

'Heavy chemicals' is a term that applies to such products as the common acids, soda ash, caustic soda and those salts and other chemicals that are produced in large quantities and at relatively little cost. The manufactures of sulphuric acid, synthetic ammonia, ammonium sulphate, caustic soda, soda ash, etc., may be cited as typical heavy chemical industries. Besides, there are a number of products which, though produced by definite chemical reactions in large quantities and at low cost, are by convention not grouped under the term 'heavy chemical industries'. One such group, for example, the manufacture of coke, gas, tar and tar products, is generally classified under metallurgical industries.

'Fine chemicals' are generally manufactured in relatively smaller amounts. Further, the manufacture requires greater skill and care in each operation under scientifically and technically trained control. Purity of the substance is much more important than the price, which is generally sufficiently great, so that it may not be necessary to take special precautions with reference to the saving of heat and power in its manufacture. Typical examples of 'fine chemicals' are some of the photographic chemicals and some highly specialised pharmaceutical products. India is backward both in the field of 'heavy chemical industries' and 'fine chemical industries'. In the present article we are concerned with heavy chemicals only. It should, however, be stated that the development of the heavy chemical industry is a pre-requisite for the development of fine chemical industry.

About 12 or 13 years ago, when the Indian Tariff Board examined the position of the heavy chemical industry in India, we were producing, throughout India, the following (shown overleaf) estimated amounts of certain heavy chemicals. Authoritative statistics are not available about the present production and demand. It may safely be put down at twice these figures.

Considering the above figures it is evident how hopelessly backward the position of India is in the field of manufacture of heavy chemicals. Taking the case of only one heavy chemical, namely, sulphuric acid, countries like U.S.A., England, Germany, France and Belgium,—every one of these countries

Name	Estimated production (average of five years 1923-1928)	Estimated demand
Sulphuric acid	20,000-22,000 tons	23,000 tons
Hydrochloric acid	500- 800 "	800 "
Nitric acid	500- 800 "	800 "
Phosphoric acid	13.5 tons average production per year Nobody else makes it	300 "
Zinc chloride	Our production 5.5 tons average	1,200 "
Epsom salt	2,500-3,000 tons	5,000 "
Alum of potash	800-1,000 "	4,000 "
Copperas	800-1,000 "	1,500 "
Copper sulphate	100 tons	700 "
Glauber's salt	1,000 "	3,000 "
Soda sulphide	Not definitely known We made 12 tons per year average	1,500 "
Alumina ferric	1,000 tons	
Bone superphosphate	300 "	
Bone meal	100,000 "	
Mixed fertilisers	3,000 "	
Pure products	Not definitely known 35,000 lbs is our annual average	
Alumina sulphate		4,000 "
Chemical fertilisers		30,000 tons De- mand is increasing every year.

was preparing sulphuric acid over a million tons per year. It has often been stated that foremost of the many indications that point to the industrial prosperity or otherwise of a country is the quantity of sulphuric acid produced. From this point, India perhaps occupies the bottom-most position in the world. Apart from the meagre production of the chemicals mentioned above, India is importing large quantities of heavy chemicals required by textile mills and other industries. The above figures bring out another important point, namely, that the only heavy chemicals that were manufactured in India belong to the group of sulphuric acid and articles that could conveniently be manufactured from sulphuric acid. This was due to the fact that freight on acids from foreign countries to India was very heavy and it paid the manufacturers in India, even with inefficient methods, to manufacture sulphuric acid and some other allied industrial chemicals. The absence of manufacture of alkali and alkali products is significant.

Things have changed during the last fifteen years. New industries have come into existence in India and these are making demands for heavy chemicals and their production has increased to an appreciable extent. The flotation of two large companies, one in Northern India and the other in Western India, for the manufacture of caustic soda, soda ash, bleaching powder, chlorine and some other chemicals, fills a very big gap in the region of heavy chemical industries in India. The alkali industry will be complementary to the acid industry and this consummation was long in being realised in India.

If India is not self-contained in respect of cheap alkali or alkali products, industries like glass manufacture, soap manufacture, aluminium manufacture, paper manufacture, cannot hope to thrive and prosper in the country. The textile mills also will benefit by this development. To keep pace with the combined output of alkali by these two companies, it will become necessary to increase the production of commercial acids throughout India. Many of the manufacturers of these acids are already making additions to their plants. For example, if India is to be self-contained in respect of galvanising and tin-plate industries, and also in respect of superphosphate, ammonium sulphate, etc., greater amounts of acids will have to be manufactured in the country. It is hardly possible in a short article like this accurately to estimate and describe the beneficial results that accrue to a country by the production of cheap acid and alkali in promoting a ramified and diversified system of chemical industries and also industries that require chemicals in their various processes. Without cheap acid and cheap alkali, we can never hope to start a 'Rayon industry' in India. It may be necessary to start producing carbon bisulphide—if the viscous process is to be adopted. Otherwise, we shall have to produce more acetic acid and its derivatives.

India's prosperity is ultimately bound up with agriculture. With the population, according to the 1941 census reaching four hundred million people, the problems of agriculture has become more and more insistent and important. Agricultural production in India can increase only to the extent we use artificial fertilisers, notably, ammonium sulphate, superphosphate and some others. The production and use of artificial fertilisers for increasing the agricultural production in the country are going to be the biggest factors in the national programme of reconstruction.

It has been the fashion to make this statement for over half a century, but progress achieved is negligible. To attain the desired ideal, we must increase the production of ammonium sulphate and superphosphate, which entails an enhanced production of ammonia and sulphuric acid. India is poor so far as deposits of phosphatic minerals are concerned, but by carefully conserving the bones available in the country, it is possible to manufacture all the superphosphate required by the agriculturists in India. Regarding ammonium sulphate, the present demand is estimated to be between a hundred-thousand and a hundred-and-twenty-thousand tons, and it is rapidly going up. In the by-products recovery coke-oven plants at the two iron and steel works in Northern India and in one gas-making plant at Calcutta, we are producing round about twenty thousand tons of ammonium sulphate. Recently in Mysore, the first synthetic ammonia plant has been installed with a productive capacity of 7,200 tons of ammonium sulphate. It is thus evident that even under the present conditions we are not producing all the chemical fertilisers which our country needs.

Whether for the manufacture of superphosphate or ammonium sulphate, sulphuric acid is necessary, unless the anhydrite process of manufacture is

adopted in the case of ammonium sulphate More investigation is necessary before we can depend on this process

The most important thing to remember in this connection is that India should establish a greater number of synthetic ammonia plants, well distributed all over the country to satisfy the regional demands The importance of synthetic ammonia lies in the fact that during peace-time it can give us ammonium sulphate, the most important chemical fertiliser, and during war-time nitric acid, without which there may be no modern explosive industry

Therefore, the manufacture of sulphuric acid and synthetic ammonia constitutes a key industry, in every sense of the word, to serve the needs of a country both in peace and war The modern explosive industry requires cellulose (generally in the form of cotton), glycerine, nitric acid and sulphuric acid in large quantities Accurate statistics are not available as to the quantity of explosives used in India for civil purposes (like dynamite) and also the explosives used for military purposes So far as is known, there is only one factory in India, under military control, for the manufacture of cordite By all accounts, this is a very small factory In the scheme of national defence, sooner or later, probably sooner than we think, we shall have to provide for the manufacture of explosives both for civil and military purposes The manufacture of modern explosives is a typical heavy chemical industry, even though on account of its immense proportions and military importance it is classified under its own special name

The manufacture of synthetic ammonia requires nitrogen and hydrogen. In the cost of production of synthetic ammonia, the cost of production of pure hydrogen will be the single biggest item In the scheme which I had submitted to the Government of Mysore and which was subsequently adopted by them, I had recommended the production of hydrogen by the electrolytic process, on account of special conditions obtained in Mysore and also on account of the forward policy of the Government of Mysore in promising this concern electric power at a remarkably cheap rate unheard of in India till now, i.e. 0.125 of an anna per unit The present concession given by the Government of Mysore is tantamount to a perpetual subsidy of three to three and a half lakhs of rupees to the Mysore Chemicals and Fertilisers, Ltd But for this generous help of the Government of Mysore, this first synthetic ammonia plant in India would not have come into existence three years ago.

Generally, in Western countries, hydrogen is obtained by water gas process in all large plants and by other gas recovery processes in smaller plants It is stated on good authority that nearly 75 to 80% of the synthetic ammonia plants in the world obtain their hydrogen by the water gas process. Along with any expansion of the Mysore Plant will also have to be seriously considered this source of hydrogen, since on the expansion of the present plant, it may be cheaper to obtain hydrogen by the water gas process. The new synthetic ammonia plants that will come into existence in India will, therefore,

have seriously to consider the possibility of getting their hydrogen by the water gas process. Suitable sites should be available in Bihar near the coalfields, where production of hydrogen by water gas process may be exceptionally cheap. A further inducement for the establishment of the next synthetic ammonia plant in Bihar will be the ready market for the ammonium sulphate in the extensive sugarcane fields of the Province. It is a matter for some satisfaction that the first synthetic ammonia plant and the second contact sulphuric acid plant in India, which I erected and started working, are going on smoothly under the management of technical staff consisting only of Indians. The success achieved in this plant at Mysore should hearten and stimulate other similar enterprises in other parts of India.

With ammonia obtained at a reasonable cost, nitric acid can be produced by the ammonia oxidation process easily. Sulphuric acid of the requisite strength and purity can be manufactured by contact process. Cotton of requisite quality is available in India. The only gap in this region is lack of adequate supplies of glycerine and toluene. During the last quarter of a century, India had witnessed a remarkable development in the soap industry. But with the exception of two factories, all the others are medium sized factories which do not recover the by-product glycerine. (By way of passing, it may be remarked that pure glycerine is required in fairly large quantities by the rapidly growing pharmaceutical industry in India.) So far as is known, Messrs Tata Oil Company, Bombay and Ernakulam, and Messrs Lever Bros., Ltd., Bombay, are the only two concerns that are producing glycerine, since their scale of operations in the field of soap-making permits them an economical recovery of glycerine. If we should start the manufacture of explosives in India, as we have to do in the near future, the manufacture of larger quantities of glycerine will have to be tackled without delay. It is for chemical engineers to find out if at all it is possible to devise some method of glycerine recovery even in medium sized factories. It will not be an exaggeration to say that the amount of glycerine that is now wasted in Indian soap factories is more than the demand for glycerine to satisfy the needs of India for explosives for the next 10 to 20 years. If on account of the special industrial conditions obtaining in India it is not possible to recover glycerine from the small and medium sized soap factories, we shall have to obtain the product by the fermentation process. The sooner the bio-chemist in India tackles this problem, the better and safer it will be from the national point of view. We shall have to import toluene from abroad (Borneo petroleum may be one of the sources) or we should develop the coal tar distillation industry in India. It has been stated that production of toluene will commence in Northern India very shortly.

There are a number of imported chemicals which can be manufactured in India, but the pre-requisite is the existence of a healthy and vigorous heavy chemical industry. For example, the improvement of leather tanning and manufacture depends on the use of chemicals. It is only recently that the

Government of Mysore pioneered the bichromate factory with a small output sufficient to cater to the demands of South India. Apart from the synthetic dyes, textile mills require a variety of chemicals and these in turn depend on cheap acid and cheap alkali

It has not been possible in an article like this to do more than give a bird's-eye view of some of the aspects of heavy chemical industry in India. I am quite sure that other contributors to the symposium will have done justice to the subject from other points of view

## MANUFACTURE OF GLYCERINE IN INDIA

By P A NARIELWALA, K P RAU and M P MADHAVAN, *The Tata Oil Mills Co, Ltd, Bombay*

(Read at Symposium, April 19, 1941)

### 1 *What is glycerine*

Glycerine or glycerol, to speak in terms of chemical phraseology, is a trihydric alcohol. It is usually found in combination with fatty acids in natural fats and oils. It has been the tendency to designate the name glycerine to the technically prepared pure substance which is the nearest approach to glycerol, represented by the formula,  $\text{OH} \cdot \text{CH}_2\text{CH}(\text{OH}) \cdot \text{CH}_2\text{OH}$

### 2 *Sources of glycerine*

Glycerine is a basic constituent of oils and fats, of which a large variety is available abundantly in this country. The approximate percentages of available glycerine in some of the important Indian oils and fats are given below —

Cocoanut Oil	13.5%
Mhowa Oil	9.0%
Groundnut Oil	9.8%
Tallow	9.5%
Cottonseed Oil	9.8%

### 3 *Characteristics of glycerine*

The British Pharmacopœia describes glycerine (glycerinum) as a clear, colourless, odourless, syrupy liquid, having a sweet taste, which is followed by a sensation of warmth. It is hygroscopic and is optically inactive and neutral to indicators. Its molecular weight is 92.06 and specific gravity (15.5°C/15.5°C), 1.260–1.265.

### 4 *Manufacture of glycerine in India*

The manufacture of glycerine in India is of recent origin, and is carried out at present only by two concerns, namely, the soap factories of Lever Bros (India), Ltd and the Tata Oil Mills Co, Ltd\*. Until 1934, the glycerine consumed in India was entirely imported, and it was only in the end of 1935, when Lever Bros. started to manufacture soap on a large scale in Bombay that glycerine began to be produced in India. The Tata Oil Mills also put up about

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\* Since this article was contributed, two other plants have been set up in Bombay for the manufacture of glycerine.

the same time a Glycerine Recovery Plant at their Cochin factory for the manufacture of crude glycerine, which they exported to European markets successfully until 1939, when they erected a new and up-to-date Soap Plant in Bombay, where they laid down a Glycerine Distillation Plant for the manufacture of Pharmaceutical, Commercial and Dynamite glycerine

### 5 Import of glycerine into India

The imports of glycerine into India during 1931-36, i.e. 5 years prior to the starting of glycerine production in India, and from 1936 onwards, i.e. after Lever Bros and Tata Oil Mills started manufacturing, are revealing

#### Imports of Glycerine into India

Year	Cwts	Value
		Rs
1931-32	7,687	2,65,070
1932-33	9,990	3,13,006
1933-34	11,855	3,76,743
1934-35	10,988	3,89,890
1935-36	9,838	4,27,746
TOTAL	50,358	17,72,455
Average per year	10,071	3,54,491
Average rate per cwt Rs 35 20		
		Rs
1936-37	1,956	70,376
1937-38	1,828	1,07,015
1938-39	4,189	1,97,520
1939-40 (for 9 months only)	781	36,206
TOTAL	8,554	4,11,117
Average per year	2,209	1,05,796
Average rate per cwt Rs 48		

(N.B.—The above prices are c.i.f. Indian Ports, and to them will have to be added Import Duty at the rate of 25% *ad valorem* to arrive at the market prices.)

From the above figures it would appear that when Lever Bros (India), Ltd started making glycerine, they managed to reduce the imports substantially, and with the coming on the Indian market of Tata's glycerine in 1939, the imports had virtually ceased. This is a gratifying feature, as it has provided the country with a valuable commodity, the importance of which in wartime cannot be underestimated. India would have been in an unenviable position during the present time, when Europe is engaged in a ruthless war, if glycerine were not manufactured in the country. During the last World War, when India's requirements of glycerine were met from abroad, it is reported that the price of glycerine had gone up to as much as Rs 150 per cwt. Today, in spite

of the war, the price of glycerine in India is about Rs 62 per cwt, an increase of about 15% over the pre-war price. This increase was necessitated to cover the higher cost of chemicals, packing materials and labour which the war has brought about.

#### 6. *The method of recovery of glycerine*

The liberation of glycerine from oils and fats can be effected by several processes. The method adopted in India so far is to recover it from the spent lyes which are produced in the course of soap manufacture, by what is known as the 'Settled Process'. When oils are saponified with caustic soda by steam, the fatty acids present in the oil combine with the caustic to form soap. The soap is thereafter washed by a salt solution to free it from glycerine and other organic and inorganic impurities that are present in the oils saponified. On settling the mass, the soap floats, whilst the spent lye containing glycerine, salt and impurities is run down from the bottom of the soap pans to the glycerine recovery plant for purification and concentration. The glycerine content in the spent lye varies from as low as 4% to as high as 11%, depending upon the glycerine content of the raw materials employed in the manufacture of soap and the care and skill bestowed in the manufacture of soap and in the production of lye in relation to the weight of oils taken for saponification. Since glycerine is a by-product of the soap industry, the requirements of the soap boiler usually determine the choice of the oils and fats, and this in turn is conditioned by the cost and the soap-making qualities of the oils and fats used. The efficiency of glycerine recovery, therefore, depends to a large extent upon the thoroughness with which the washing of soap is carried out in the pan, as also upon the purity of the raw materials used, since the impurities present in the raw materials will necessarily find their way into the spent lyes.

#### 7 *Availability of glycerine in India*

The production of soap in India is estimated at about 90,000 tons per annum. Assuming that the major portion is made by cold and semi-boiled processes, the glycerine that ought to be available for recovery from the Settled Process of manufacture should work out to at least 2,500 tons per annum, but even this quantity is not produced, and the present production of glycerine in India is estimated at about 1,000 tons per annum. Unfortunately, in India the manufacture of soap by the Settled Process has not advanced rapidly enough due to the facility with which soap can be made by cold and semi-boiled processes which need little or no equipment, and which can, therefore, be made on cottage industry scale. With the recent attempts to revive village and cottage industries in India, the manufacture of soap on cottage basis is likely to get an impetus to the detriment of a valuable by-product like glycerine. Thus a good portion of the recoverable glycerine that is already running to waste will continue to run to waste on a still larger scale.

The cottage factories have neither facilities nor technical skill to make soap by the Settled Process or to evaporate the spent lyes. Even in small factories where soap is made by the Settled Process, the installation of glycerine recovery and distillation plant is not an economic proposition, and unless the soap industry in India is organised on a better basis (particularly if the small sized plants are made to realise the importance of working together) the recovery of glycerine by small factories will not be worth their while. As the demand for glycerine in India is likely to increase with the development of new industries, a larger production of glycerine can only be had either by the establishment in different parts of India of large size soap factories, capable of manufacturing soap by the Settled Process, or by getting the smaller soap factories to agree to send their soap lyes to large central glycerine recovery plants, or by the development of a new industry in India, viz the manufacture of fatty acid by the splitting of oils. It may not be out of place to mention that on the one hand we are running to waste soap lyes which are rich in glycerine and on the other we are importing lakhs of rupees worth of pharmaceutical and toilet preparations in which glycerine is an ingredient in one form or another. The sales of imported pharmaceutical preparations in India are on the increase, whilst toilet preparations which are meant to enhance 'my Lady's' charm and complexion seem to be growing in popularity with the women of the country.

### 8 *Other methods of recovery*

Before detailing the method of treatment and evaporation of the spent lyes for the manufacture of glycerine, it might be advisable to consider the three other methods which find favour for the recovery of glycerine. These methods are —

- (1) the Autoclave method,
- (2) the Twitchell process, and
- (3) the Fermentation method

In the Autoclave process, the oils and fats are boiled with steam under pressures of 6 to 10 atmospheres, with lime, magnesia, zinc oxide or zinc dust, whilst in the Twitchell process, the hydrolysing agent is a special reagent named after its inventor Twitchell and the operation is conducted at atmospheric pressure. By these processes, a higher recovery of glycerine than from soap lyes is feasible, since in the manufacture of soap a certain amount of glycerine is always left over in the soap in spite of all the care and technical efficiency that can be brought to bear in its manufacture. But these two processes, however, have a serious disadvantage in that, during the process of splitting the oils, the resultant fatty acids are of a dark colour and cannot be used directly either in the soap or any other industry, unless distilled under a high vacuum. The third or the Fermentation method needs special consideration in India, as an enzyme isolated from castor seeds which are available

in plenty in India forms the hydrolysing agent in this process. This method has also a greater advantage over the other two processes, due to the fact that the capital outlay is comparatively small and the resultant fatty acids are sufficiently light coloured for direct use in the manufacture of soap. The only disadvantage with this process is the purification of 'Sweet Waters' which requires a little extra care and skill. With the industrialisation of India, and particularly with the growth of the cosmetic industry, the demand for a high quality stearine—a commercial mixture of stearic and palmitic acid, with a small proportion of oleic acid—is likely to steadily increase, and one or the other of these processes is therefore likely to be developed for the manufacture of stearine in India within the next few years. Mhowa and cottonseed oil, amongst other Indian vegetable oils, appear to be suitable raw materials for the manufacture of stearine, as they are rich in palmitic and stearic acids.

### 9 *Quality of spent lyes*

It would be obvious that, if the evaporation costs are to be kept low, considerable attention must be paid to see that the spent lyes are rich in glycerine. Also, to keep the treatment cost within reasonable limits, the spent lyes should be free or very nearly free from caustic alkali, organic impurities, carbonates, etc. As stated earlier, a certain amount of impurities are inevitable in the lyes, as they are the impurities which are present in the oils and fats and which must necessarily find way into the lyes when soap is being washed with the salt solution. Again rosin (which forms an important ingredient in the composition of many grades of soap) with its impurities gets into the glycerine plant in spite of all care. Thus, when the spent lyes are transferred to the glycerine plant from the pan room, they contain, in addition to salt and glycerine, a small percentage of dissolved soap, other organic impurities, carbonates, etc. The efficient working condition in a pan room, however, will yield spent lyes with a high percentage of glycerine and free from, or containing as little as possible of, alkalis, carbonates, organic matter, etc.

### 10 *The treatment and evaporation of lyes*

The treatment of lyes consists in removing the various impurities like carbonates, etc from them. The treatment and evaporation of lyes are carried out under three distinct operations. In the first operation, the alkalis and most of the organic impurities are precipitated with the help of chemical reagents like aluminium sulphate or ferric chloride with hydrochloric acid. After treatment with these reagents, the lye is filtered and treated with caustic soda to remove the excess of aluminium or iron present. This is the second operation. It may be stated here that the comparatively high cost of hydrochloric acid, and therefore of ferric chloride also in India, acts as a great handicap in the treatment of lyes, and if they were available at a cheaper price, the use of aluminium sulphate could be completely dispensed with,

since this reagent ultimately reduces the purity of the salt recovered and thereby affects the efficiency of graining of soap. It should also be borne in mind that the chemicals used, particularly the acids, should be absolutely free from arsenic and lead, as once the impurities are introduced in the system, it is difficult to get rid of them during any subsequent stages. The stringency of the B.P. specification for chemically pure glycerine regarding arsenic and lead can be judged from the following stipulations laid down —

Limit for arsenic 4 parts per million

„ „ lead 1 part per million

The treated and purified lyes are now ready to be taken into the evaporators for the third and final operation. In the earlier days, it was the practice to evaporate the lyes on open hearths and to concentrate them up to about 80% glycerine content. With the introduction of vacuum evaporators, great economy in recovery as well as fuel consumption has been effected in the concentration of lyes, and today evaporators ranging from single, double and multiple effect are in use for the concentration and evaporation of lyes. The popular type is the double effect evaporator, in which stepping up the vacuum in one of the vessels enables the vapours from the other to be economically used for purpose of evaporation. As the major part of the water present in the lyes evaporates, the salt from the lyes settles out and is collected in special salting-out boxes fixed to the bottom of the vessels. The evaporation is continued till the glycerine content in the lye reaches about 80%, and this product constitutes the 'crude' glycerine of commerce. This crude glycerine contains 80% glycerol, 8–10% salt and 1–3% organic impurities with a little water.

## 11 *Distillation of crude glycerine*

The crude glycerine is distilled in a separate distilling unit for the production of industrial pale straw, dynamite, C.P. and other qualities of glycerine. Pure glycerol boils under atmospheric pressure at about 290°C, whereas at lower pressures it distils at lower temperatures. A higher vacuum, however, gives an improved product and this point has received merited attention in the design of modern plants. The modern tendency is to distil with the aid of superheated steam under a very high vacuum of 6 to 9 mm, which would permit of distillation below 200°C. By suitably adjusting the temperature of the condensing vessels, pure glycerine is condensed and recovered. On distilling the 80% crude, a product of a pale yellow colour is obtained as the first distillate. This product contains 99 to 100% glycerol and has a sp. gr. of 1.262 to 1.265. This constitutes the dynamite or the industrial pale straw glycerine of commerce. By further distillation and purification (by means of bleaching carbon), chemically pure glycerine satisfying the rigid specifications laid down in the British Pharmacopœia is obtained. The final glycerine as it comes out from the distillation plant is then packed in tins or galvanised

drums and is ready to go out to the market. A large amount of care is necessary in the process of distillation, particularly with regard to the removal of free fatty acids. Although the British Pharmacopœia has not laid down any limits with regard to the presence of free fatty acids, it has been found in practice that to produce an odourless glycerine, the limit of free fatty acids should not be above 0.01%, as otherwise they give a smell to the glycerine which is considered objectionable. With judicious care in the treatment of crude glycerine, as also in the process of distillation, the trouble regarding the presence of free fatty acids can, however, be easily overcome.

## 12 *Foots*

In the process of distillation a certain tough plastic substance is left in the still as a residue, which is known as 'foot'. The dry foot on analysis is found to contain about 60% of ashes mainly composed of sodium chloride and sodium sulphates. The balance of 40% consists of a mixture of glycerol and condensation products of glycerine, such as poly-glycerols. The use to which the foot can be put has remained a tough problem and awaits a solution by research chemists.

## 13 *Uses of glycerine*

The following properties of glycerine will give an insight as to its possible use in the various industries —

- (a) It has a sweet taste
- (b) It is highly hygroscopic and on exposure to the atmosphere, takes up as much as 50% of its weight of water
- (c) It has powerful solvent properties, and when mixed with water, improves the solvent property of the latter
- (d) It acts as an antiseptic even in dilutions up to about 12%

The largest use of glycerine ordinarily in India is in the pharmaceutical industry and medical stores, and to some extent in the manufacture of toilet preparations, but since the beginning of the war, it finds a ready and larger application in the production of dynamite and other explosives for defence purposes. Today perhaps its important consumer is the explosive industry, next to which comes its use in the pharmaceutical industry. Many tonics, wines, liquors, contain glycerine because of its smoothening, sweetening and preservative properties. In the tobacco industry, it is used to keep the tobacco moist, sweet and also to act as a partial antiseptic. In toilet preparations and cosmetics, it finds extensive use, as it imparts to the skin 'brilliance, softness and delicate colour'. Its hygroscopic nature is taken advantage of for keeping articles soft and pliable and also to prevent their drying up. It is used for keeping wood, leather, paper, etc. soft and pliable and also for keeping moist, copying and printing inks, blacking, etc. Due to its high solvent action, it is used as a solvent in extracting perfumes and alkaloids.

#### 14 *Other possible uses*

There are one or two directions in which the use of glycerine can be extended in the Indian market. In the textile industry, large quantities of 'wetting' agents are in use for keeping the fabrics of cotton threads in the moist condition. Judicious use of glycerine in such preparations should find increasing favour with mill technicians. In tobacco curing, jaggery water seems to be in use for preserving the moisture in the leaf. Here also glycerine can very advantageously be used. In these instances, a proper guidance in the use of the right article for the right purpose is all that is needed.

#### 15 *Post-war problem*

When the present World War II ends, the problem of finding new uses for glycerine will be of increasing importance, and an opportunity presents itself to research chemists to work from now onwards in finding ways and means for using glycerine in different industries for different purposes. The existing limitation of demand will soon serve as a check on a larger production of glycerine. It is in the interest of the Indian industries in general and the glycerine industry in particular that steps should be taken to tackle these various problems. Recent patent records and industrial magazines refer to various uses of glycerine. This information should be made the basis for conducting further investigations for evolving new uses for glycerine to suit Indian manufacturing conditions.

# POSSIBILITIES OF HEAVY CHEMICAL INDUSTRIES IN THE PUNJAB

By J L SARIN

(Read at Symposium, April 19, 1941)

The importance of heavy chemicals to the various industries<sup>1</sup> of the country is illustrated graphically in fig 1. This figure also shows the

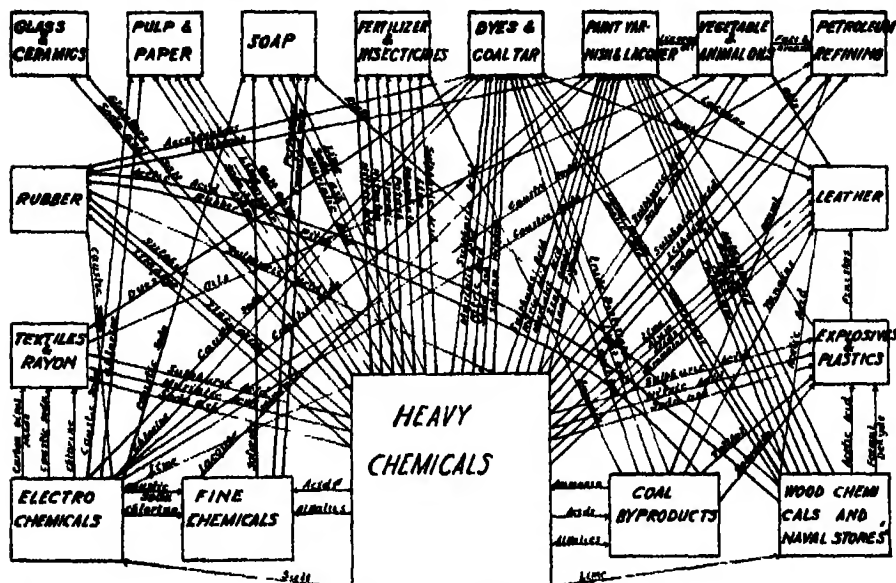


FIG 1 INTERINDUSTRY MOVEMENT OF PRINCIPAL RAW MATERIALS  
OF CHEMICAL ENGINEERING INDUSTRY

inter-industry movement of principal raw materials of the chemical engineering industries. It will be seen that the most important raw materials for heavy chemical industries are (1) Salt, (2) Limestone, (3) Sulphur, (4) Coal, and (5) Ammonia. All of them are found in the Punjab and can be used for the development of heavy chemical industries as would be seen from what follows immediately below —

1 **Salt**—Common salt is the starting point for alkali industry. The relationship of alkali industry to modern industries<sup>2</sup> is illustrated in fig 2. The Punjab salt mines, situated in the Salt Range, produce about 150,000 tons of salt per year. Of them the principal is the Mayo Salt Mines at Khewra in which there lies a purely crystalline salt of light pink colour interbedded with some seams of impure red earthy soil (*kalar*) of the total thickness of 300 feet. Above this there is another bed of the thickness of about 250 feet. The upper deposit is not so pure as the lower, for it contains more intercalation of *kalar* and is associated with other salts, e.g. calcium sulphate, magnesium, potassium

and calcium chloride in great proportion. The lateral extension of the salt beds appear to be very great extending to several square miles in area. There

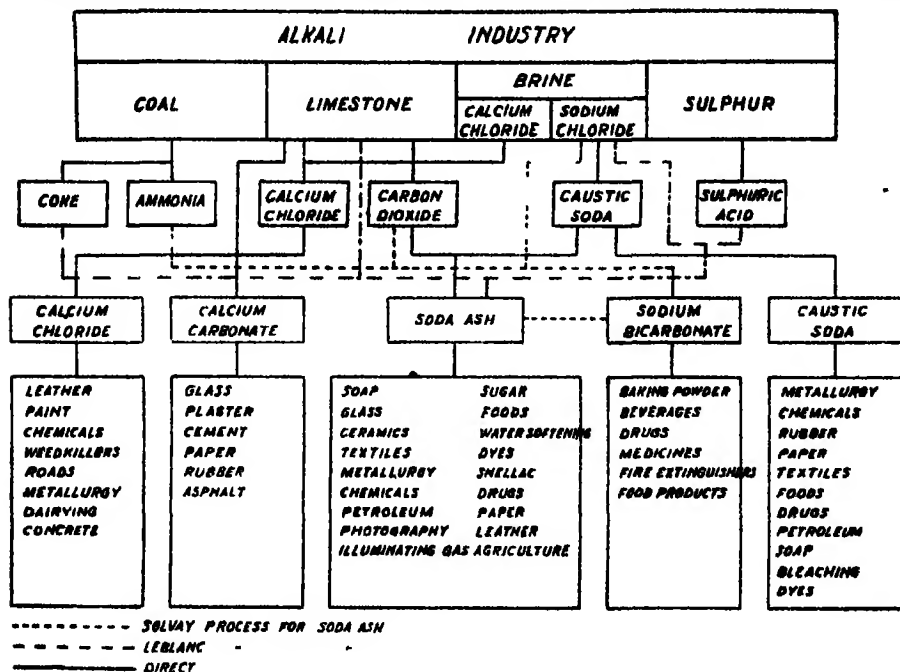


FIG 2 RELATION OF ALKALI TO MODERN INDUSTRY

is thus a very large supply of salt from the Khewra deposits. Until recently the entire salt was distributed all over Northern India for edible purposes. Now a large factory is being erected by the Imperial Chemical Industries for the manufacture of soda ash from this salt at Khewra. When this factory starts producing soda ash, a number of industries which consume soda ash would grow and the existing ones would extend, resulting in the subsequent development of the alkali industry itself. Of these industries, the glass and soap industries are the most important. There were numbers of glass factories working in the Punjab, but on account of difficulties in securing supplies of soda ash most of them have closed down.

The Imperial Chemical Industries do not propose to produce any caustic soda in the Punjab. If my information is correct, I understand they are putting up a caustic soda plant at Calcutta. Those who have seen the Salt Range might have noticed that a very concentrated brine is pumped out ruining the agricultural fields round about the mines. It is not known whether the Imperial Chemical Industries propose to use the waste brine, in case it is found suitable for the electrolytic decomposition.

2 *Lime*—Lime is a primary material of great importance in chemical industries. Its utility lies in the fact that being the cheapest form of alkali it has extensive application, as in conversion of sodium carbonate to caustic

soda, in the liberation of ammonia from ammonia salts, in the purification of sugar and in the manufacture of dyes intermediate

Limestone of great purity is found abundantly in the Salt Range. At present it is mostly used for the production of quick lime for building trade. Some whiting is also prepared from it.

Lime is also used in the manufacture of Portland cement. One factory has already been working for the manufacture of this article for some time past and another factory has recently been started. There are, however, still greater possibilities for the utilisation of this raw material in the manufacture of cement of various other kinds.

3 *Coal*—Coal is a raw material on which the industrial supremacy of a number of countries, particularly Great Britain and Germany, has been established. India is also a large producer of coal, but we have not exploited it for the industrial growth of our country to the same extent to which other countries have done. As a fuel it is required directly or indirectly by almost all industries. In the Punjab the coal deposits are not very extensive, the annual production is only a few thousand tons. All the coal produced is at present used in firing brick kilns, etc. Sample of this coal was sent to England and the analytical examination showed that this coal was very suitable for low temperature carbonisation. Within the last forty years, specially since the last war, increasing attention has been given to methods whereby coal can be converted into smokeless fuel and also may yield valuable by-products, particularly oil. It appears that the possibilities of starting low temperature carbonisation for production of crude coal tar, smokeless fuel, crude petrol and other products are bright in the Punjab. The Punjab coal is known to possess high percentage of sulphur<sup>3</sup> and the recovery of this material, if ascertained to be a possibility, may form a source of this important

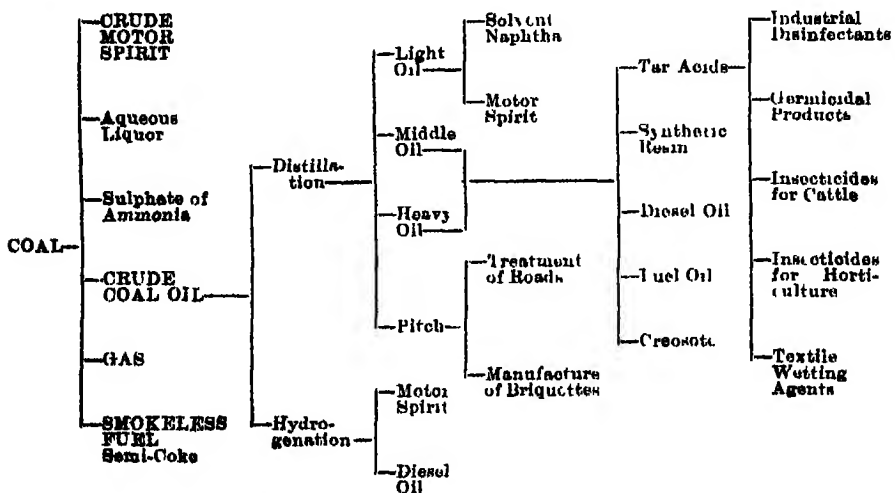


FIG. 3. Low Temperature Carbonisation of Coal.

raw material. The different products that can be obtained from low temperature distillation<sup>4</sup> are illustrated in fig 3. The Punjab Government has recently sanctioned a sum of Rs 10,000 for carrying out research in this direction, and it is hoped that as a result of this work, coal distillation would be started in the Punjab in the near future.

4 *Sulphur*—Sulphur in its natural form is not found in the Punjab. As in the case of other provinces of the country, the natural consequence is that sulphuric acid cannot cheaply be manufactured in the Punjab. There is, however, one redeeming feature, that is, in the Punjab gypsum and pyrites are known to be found in abundance. Gypsum is found in the Salt Range and pyrites deposits are found in the Simla hills, and in the form of pyritous shale at Kalabag and Dandot collieries in the Salt Range. Some deposits of pyrites have also been located in the Kangra valley and a representative sample collected by a member of the staff of the Industrial Research Laboratory is under examination. Neither has any attempt been made so far nor any investigation undertaken to study the economic production of sulphuric acid from gypsum. Pyrites found in the Simla hills are now used successfully in the manufacture of sulphuric acid in the adjoining province of the U P at Agra. The presence of sulphur has recently been located in Baluchistan by the Geological Survey of India. Wadia, in his book on 'Geology of India', mentions the occurrence of sulphur in Baluchistan<sup>5</sup> and Cumming in his monograph on 'Suggestions for the Industrial Development of Baluchistan' has described the occurrence of sulphur in workable quantities at Siln and a number of other places.

It appears that in the Punjab hills, particularly Himalayas, extensive amount of pyrites exist, and if they are properly exploited, the absence of sulphur as the primary raw material for the production of sulphuric acid would not be felt, and the Punjab would be able to produce sulphuric acid cheaply.

In the foregoing I have dealt with two principal sections of the heavy chemical industries, namely, alkali and acid industries. Besides these, there are a few other raw materials which can be used for the development of some other important sections of heavy chemical industries. Of them the most important are salts of potassium, borax, ammonium and magnesium.

*Potassium Salts*—After Bihar, the Punjab is the most important province in which saltpetre or potassium nitrate is collected. Saltpetre is the natural product formed in the soil of alluvial districts by natural process under peculiar conditions of climate prevailing in these districts. Exact figures of production of this important salt are not available, but there is a belt which runs across in the centre of the province starting from the Salt Range in the Kalabag district to Delhi in the south. In this area there are about 10 to 12 factories which work to produce saltpetre of sufficient purity. Besides this source of potassium salt, there are found in the Salt Range some other salts of potassium of which the most important are kainite, blodite, etc. None of these salts are at present put to any economic or industrial use and the possibilities

of starting the industry of potassium salts for use as fertilisers and manufacture of explosives require consideration. It appears that caustic potash and potassium chloride could be produced from these sources.

The possibilities of manufacturing pearl ash from organic sources, e.g. the forest undergrowth and waste, have been investigated and it has been found that in some of the districts of the Punjab, particularly Simla and Kangra, its production can be organised on commercial scale during the present days of war. The industry can be developed successfully and recently a demonstration party has been organised to work in this district with this end in view.

*Borax*—Borax as a raw material is not found in the Punjab, but the industry of refining borax has been carried out in the town of Jagadhari from very old times. Borax, which occurs as a natural salt, is obtained from lake deposits of Tibet and Kashmir. Before the advent of the imported material there were working in this town of Jagadhari about one dozen factories producing 30 thousand maunds of borax per year, but now they have all stopped working and recently an attempt has been made to revive this industry by introducing better methods of refining and recrystallising this material so as to produce a product which can match foreign one.

The possibilities of preparing boric acid from borax by decomposing this chemical with hydrochloric acid and sulphuric acid are being investigated and if the process can be worked commercially, it will be introduced in the province. The importance of borax industry need not be stressed, since there is no other source in Northern India from which this material can be made available at present, and the industry requires encouragement.

*Ammonium Chloride*—Salts of ammonia are of great importance and specially in these days of war no country can afford to be without them. In India the sources of supplies of ammonia salts are very limited and the development of this industry has not been considered from national point of view so far. In the Punjab the supplies are almost restricted. In spite of the fact that the Punjab has good coal for distillation, no coal distillation plants have been installed there. The Punjab has thus been deprived of the advantage of supplying ammonium sulphate to other provinces of the country. To compensate this loss, however, we had in a particular area of the province an industry which produced ammonium chloride from very old times. This industry has, however, died out due to foreign competition and recently efforts have been made to revive it. Ammonium chloride is collected in raw form from old brick kilns. The mechanism of the process is under investigation. It cannot be said whether it is obtained from the clay which is used in making the bricks, or the fuel which is burnt to fire them. The production of ammonium chloride on systematic lines has, however, been started. Ammonium chloride of good purity has been produced and marketed. Due to success the industry has met, the production of ammonium chloride from ammonium sulphate and sodium chloride has also been taken in hand. This was necessary due to large demand of the salt which has recently arisen and due to the paucity of supplies of raw

ammonium chloride that can be collected from indigenous kilns. These kilns which had practically been lying idle have now again become active and it is hoped that if the study of the mechanism of the process of production of ammonium chloride provides a workable clue, a new type of tunnel kiln may be made by which the process of production can be modernised.

**Magnesium Salts**—In the Salt Range, intermixed with salt bed, are also found certain salts of magnesium of which the most important are epsomite, kieserite and glauberite. The extent and workability of these deposits have not yet been investigated.

The products of heavy chemical industries find use in a number of chemical industries. The inter-industrial movement of the raw materials produced by these industries have been shown in fig 1. It will be seen that the most important industries which use products of the heavy chemical industries are glass and ceramics, pulp and paper, soap, paints, varnishes and lacquers, vegetable and animal oils, petroleum refining, leather, wood chemicals, naval stores, textiles and rayons, explosives and plastic materials, dye products, fine chemicals, electro chemicals, and rubber. With the exception of the last seven industries, all other industries have developed to some extent in the Punjab. If heavy chemicals can be made available abundantly and cheaply, the development and growth of these industries would be multiplied, since the primary raw materials on which these industries are dependent are all found in the province in large quantities. Their location in proximity to each other is another important factor which would stimulate the growth of these industries.

As stated above almost all the raw materials are found in the Salt Range which is an ideal locality for the growth and development of these industries. Already the industries for the manufacture of soda ash and cement and petroleum refining have been built up in this locality. Besides, there are numbers of other industries, of which coal distillation, dye products, fertilisers are the most important, that can also be developed there. The Salt Range, which presents from a distance the appearance of 'ruined walls and fortification', treasures in its heart raw materials of great industrial value which are easily approachable and extractable in immense quantities. In any other country of the world, such a locality would hum with industrial life and activity, but in the Punjab, in tune with other national institutions, this locality lies passive and dormant waiting perhaps for some distant but bright future.

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# MANUFACTURE OF MAGNESIUM CHLORIDE AND OTHER ALLIED PRODUCTS AT KHARAGHODA BY THE PIONEER MAGNESIA WORKS, LTD

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*(Read at Symposium, April 19, 1941 )*

'Bitterns' is a term applied to the residual mother liquors left in the salt pans after sodium chloride (common salt) is formed. This is generally found in the ratio of 1 to 12 at Kharaghoda where the manufacture of salt on a large scale is carried on under the control and supervision of the Salt Department of the Central Government. The mode of manufacture at Kharaghoda differs considerably from the method in vogue at other places in India and elsewhere, where ordinary sea water is used. Kharaghoda forms part of the Runn of Cutch, and is only twenty miles away from the important Railway junction of Viramgam with which it is connected by a broad and metre gauge line of the Bombay, Baroda and Central India Railway Company.

The Pritchard Salt Works of Government at Kharaghoda were first opened about 75 years ago and are now giving an average annual production of about 30 to 40 lakhs of Bengal maunds of what is known as 'Badagra' salt. The whole of this area is practically a sandy desert extending right up to the borders of Sind, and was probably submerged in bygone ages, and the sea has now receded to the Gulf of Cutch situated about 60 miles away from Kharaghoda Agurs.

Salt manufacture begins at Kharaghoda soon after the rains, when the brine with which the sandy soil is saturated is raised from shallow wells and filled into salt pans to a depth of nine inches to a foot and is allowed to evaporate for a period of from six to eight weeks. Thin incrustations of salt are formed at the bottom and the floating bitterns, or waste mother liquor, is then drained off into separate channels known as 'farans'. Fresh brine is then slowly added until actual salt cubes are formed and are ready for extraction and storage to the Central Government Stores by April. The Salt Works, which are divided into a number of 'sidings', are served by a net-work of railway lines and are a regular hive of industry during each working season giving employment to several thousand labourers. Several engines, each drawing a load of 40 to 50 wagons laden with salt ply from sunrise to sunset until all the salt is removed from the Agurs and stored in the closed and open Government stores near the Railway station some few miles from the Runn. The rainfall averages only about 20 inches annually but this is sufficient to flood the low-lying Agur area in the monsoon. During the summer months the sun is very

hot, the day temperature rising up to  $120^{\circ}\text{F}$  and dust storms are frequent, but the cold weather is healthy and bracing

The 'bitterns' which are drawn off to the extent of several thousand tons annually during the salt season are extremely rich in magnesia salts, and are largely utilised for the manufacture of magnesium chloride. This is an indispensable ingredient of daily use in the sizing of yarns in textile mills and is also largely required for mixing with magnesite for purposes of jointless flooring (composition as well as for the manufacture of magnesium carbonate, calcium chloride, 85% magnesia (for boiler coverings) and other important uses

The 'bitterns' left in the pans after the manufacture of common salt from sea water contain several important salts, but, as the following analyses will show, there is a greater concentration of both common salt and magnesium chloride contents in the land bitterns and brines derived from the Runn of Cutch as compared with direct sea water. It may be mentioned, however, that the brines vary considerably in composition even in adjacent wells and the figures given in the following table are only the averages of a few samples analysed at the Government Laboratory, London, on behalf of the Director of Industries, Bombay. The figures for sea water are based on the well-known analyses of Dittmar

*Composition of the Kharaghoda brines and those derived from sea water*

	Kharaghoda brines	Sea water
	Per cent	Per cent
Sodium chloride ( $\text{NaCl}$ )	14.67	2.72
Magnesium chloride ( $\text{MgCl}_2$ )	4.63	0.33
Magnesium sulphate ( $\text{MgSO}_4$ )	0.48	0.22
Calcium sulphate ( $\text{CaSO}_4$ )	0.44	0.13
Potassium chloride ( $\text{KCl}$ )	0.41	0.07
Calcium carbonate ( $\text{CaCO}_3$ )	0.01	0.01
Magnesium bromide ( $\text{MgBr}_2$ )	0.07	0.01

'Bitterns' contain all the above salts except the calcium sulphate, and recently efforts have been made to utilise them to best advantage. At the end of each season they are usually washed away by the rain.

Magnesium chloride, magnesium sulphate (Epsom salt), potassium chloride and bromine are all substances of great commercial value, and the quantities annually wasted in India have been roughly estimated by Watson and Mackenzie Wallis as follows —

*Amount of salts wasted annually in Indian 'bitterns'*

	Tons
Magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ )	1,93,000
Magnesium sulphate or Epsom salts ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ )	1,27,000
Potassium chloride ( $\text{KCl}$ ) ..	20,000
Bromine ( $\text{Br}$ ) . . . . .	1,800

## MAGNESIUM CHLORIDE

Before the last World War magnesium chloride was practically a German monopoly, Indian supplies being almost wholly imported from Germany at a very low price of Rs 3 to 4 per cwt. At Stassfurt in Germany there are large deposits of the mineral known as carnallite, which is a double compound of potassium and magnesium salts with traces of bromides and iodides. Magnesium chloride forms the greater portion of this carnallite and has to be eliminated before recovery of the potassium bromides and iodides, so that it could be advantageously exported as a by-product at comparatively little cost, especially when it could also be shipped as bottom cargo at low freight rates.

Magnesium chloride is one of the five most important ingredients used in size mixing. All grey yarns before passing into the loom-shed require to be sized to an extent varying with the nature of the cloth to be woven and according to prevailing climatic conditions, but in order to keep the thread pliable and soft and to enable it to withstand the strain involved in the process of weaving, a certain amount of size must always be needed.

The following are the most important sizing substances in use —

- (a) Adhesive or starchy ingredients, like wheat flour, maize starch, or farina,
- (b) Weight-giving products, like China clay and French chalk,
- (c) Fatty or softening substances, like oils, beef and mutton tallow, glycerine, soap, etc.,
- (d) Zinc chloride, to prevent mildew or fungus growths, and
- (e) Deliquescent agents, like magnesium or calcium chloride for keeping the thread pliable and soft. Magnesium chloride, being highly hygroscopic, is peculiarly suitable as a sizing material.

At Ahmedabad, where the climate is for the most part very dry and hot and much heavier sized cloth is woven, there is naturally a greater consumption of magnesium chloride than in Bombay, where the climate is humid and the cloth is finer than that made at Ahmedabad. The consumption usually varies from about 5 tons per 100 looms per annum in Ahmedabad to about half that quantity in Bombay and elsewhere according to climate and the size percentage given and whether there is night-shifts working or otherwise.

Taking the total number of looms in India at about 200,000 and estimating about  $3\frac{1}{2}$  tons per 100 looms per annum as the average mean consumption, the annual requirements of the country for textiles alone may be roughly about 7,000 tons. These were practically wholly supplied from Germany before the last World War. But as soon as hostilities started and supplies were gradually cut off, a stimulus was given to the investigation of local resources and attention was drawn to the almost unlimited supply of 'bitterns' at Kharaghoda running to waste from year to year, with the result that experiments were conducted to test the possibility of turning out a good substitute for the German article.

### MANUFACTURE OF MAGNESIUM CHLORIDE IN INDIA

Tenders were invited by the Government of Bombay for the right to remove the 'bitterns' from the Pritchard Salt Works at Kharaghoda for the manufacture of magnesium chloride and other products, and Mr P V Mehd, M A, B Sc, who was then working as an Assistant Professor of Chemistry at St Xavier's College, obtained the first contract for the extraction and removal of the 'bitterns' for the year 1915 on payment of 8 annas per cwt as royalty to Government. Fresh tenders were subsequently invited for a further one year's period and a private firm under the name of the Pioneer Magnesia Works in partnership with the Hon'ble Sardar Sir Rustom Jehangir Vakil, mill-owner and merchant of Ahmedabad and Messrs P V Mehd and B S Lalkaka took up the manufacture on payment of Government royalty which was then fixed at Rs 1-8-0 per cwt.

As the first contracts were only given from year to year, it was not possible at the outset to work on a large or a permanent scale, and during the first years the crude 'bitterns' were railed from Kharaghoda to Ahmedabad, a distance of about 60 miles, and further treated there in a rough way for the use of the mills. Subsequently, however, the factory was removed to Kharaghoda where, however, on the grant of a long-term agreement from the Government it has been working successfully for the last 25 years or so.

The factory covers a very large area of several thousand yards leased from Government on which are situated their main plant and buildings, as well as officers' bungalows and workmen's chawls, drum-making plant and store houses, etc and for the stacking of many thousand drums annually made, and big reservoirs paved and cemented are also constructed to hold a large supply at hand of the raw material and for other work. A stock of several thousand drums of the finished product is always maintained to meet the demand. The plant was first designed in consultation with the Principal of the Victoria Jubilee Technical Institute, Bombay, and subsequently it was thoroughly overhauled and re-designed as per valuable advice and guidance received from Mr Kapilram H Vakil, M Sc Tech (Manc), F I C, M I Chem E., the well-known Chemical Engineer and Technologist. Mr Fakirji E Bharucha, L M E., M I Mech E (Lond), M I E, Consulting Engineer, also tendered useful advice as regards fuel problems.

### OPERATIONS AT KHARAGHODA

The first stage of operations at Kharaghoda is the collection of 'bitterns' at the source and their transport and collection at the factory. As the 'bitterns' concentrate further in the reservoirs their collection is carried out considerably in advance of their utilisation at the factory. Even at a density of 48°T the 'bitterns' still contain some common salt, and the manufacturing operations are designed to eliminate this and other salts, as well as suspended clay and like impurities. The latter settle down in the reservoirs along with

the common salt, and the resulting liquor rich in magnesium chloride is then pumped into a series of copper pans placed over furnaces and heated to the requisite density by means of concentrated fire and the flue gases until it is finally recovered and poured into drums where it quickly solidifies and is ready for removal

Analysis made on various occasions by competent chemists, both here and in Europe, would show that the Indian magnesium chloride is equal in quality and strength and colour to the best obtainable anywhere, and in price also it compares very favourably with any imported article and it has succeeded in ousting the foreign material to a very great extent

Besides capturing the bulk of the Indian market, the Pioneer Magnesia Works, Ltd have succeeded in popularising their magnesium chloride in Great Britain and in other parts of Europe and Australia where before the present war considerable quantities used to be shipped, but which are now practically stopped owing to hostilities and want of shipping

#### OTHER MANUFACTURE

The Pioneer Magnesia Works, Ltd also owned another big chemical plant at Mithapur near Okha Port in Kathiawar for the production of magnesium chloride and other by-products including Epsom and potash salts. But subsequently with the opening of the Tata Chemicals, Ltd there on a large scale for the production of soda ash and a dozen other allied chemical products, the company's activities are now confined only to Kharaghoda.

Amongst the other important products manufactured at Kharaghoda besides magnesium chloride on a large scale, may be mentioned table salt, magnesium sulphate, magnesium carbonate, 85% magnesia for boiler covering and lagging, and calcium chloride, potassium chloride and bromine. The company has spared no effort nor stinted money in carrying on the necessary research at a cost of thousands of rupees and they have always freely supported and endowed research scholarships whenever any suitable opportunity occurred



# ACTIVATION AND CLARIFYING PROPERTIES OF FULLER'S EARTH

## PART VII. ACTIVATION OF FULLER'S EARTH

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(Read at Symposium, April 19, 1941)

In previous parts<sup>1</sup> the fuller's earths from different sources in India as well as from foreign countries were tested for their decolorising properties. It was found that the *pH* of the extract, obtained by shaking a quantity of the earth with sodium chloride solution, showed close relationship with the decolorising power of the earth the higher the decolorising power, the lower the *pH* of the extract. This relationship held in the case of all samples of the earth whether raw, acid activated, electrolysed and electro dialysed or dehydrated to different extents. The inverse proportionality between the bleaching value and the *pH* was seen from the constancy of the proportionality factor (*pH* × decolorising power). The relationship also held in the decolorisation of two different vegetable oils.

The observed relationship between the *pH* and the activity of the earth is to be explained by the fact that the *pH* of the extract is a measure of the exchangeable hydrogen content of the earth and it is this hydrogen content which appears to be responsible for the activity of the earth.

In a study of the removal of colouring matter by fuller's earth from a vegetable oil, it was found that the colour was not totally removed by physical adsorption, since the various requirements of the Freundlich isotherm could not be fulfilled. The nature of the decolorisation curves showed that only a small proportion of the colouring matter was removed by adsorption and the rest by chemical reaction with the active element in the earth. With fine-grained earth, decolorisation could be expressed by a modification of the Freundlich equation  $x/m = ac^a + bc$ , where *bc* accounts for the chemical effect. Taking into consideration the existence of base-exchange reactions usually found in clay materials and the observed relationship between the *pH* and the decolorising power of the earth, the chemical reactivity of the exchangeable or zeolitic hydrogen in the earth with the colouring matter of the oil became obvious.

When hydrogen earths were converted into sodium, magnesium, calcium or aluminum earths by treatment with the corresponding salts, the activity of the earth was considerably reduced. The activity could, however, be restored by treating these earths with a small quantity of hydrochloric acid. The replacement of the bases by hydrogen could also be effected by subjecting the earth suspension to electrolysis or electro dialysis, when calcium, sodium

and aluminium could be found extracted in the wash and the decolorising power of the earth increased. The electrolytic activation of the earth could be augmented by addition of small quantities of acid which helped towards further extraction of the bases. The activity of the earth was found to have no relation with the exchangeable calcium as postulated by Folge and Olin<sup>2</sup> or with the combined action of exchangeable aluminium and hydrogen as suggested by Hofmann and co-workers<sup>3</sup>.

The activity of the earth was, however, found to depend on the nature of the essential mineralogical constituent of the earth as found by Hofmann. From the nature of the dehydration curves and their comparison with those of well-known clay minerals, the earths could be classified with regard to their mineralogical origin. Active earth showed high proportion of montmorillonite, while in the less active ones kaolinite predominated. The higher activity of the montmorillonite earth is in agreement with the fact that montmorillonite is characterised by a high zeolitic exchange. From the rate of dehydration and the amount of water loss, the two types of water, namely, adsorbed water ('planar' and 'broken-bond' water) and the crystal lattice water derived from the H and OH planes, could be distinguished. A study of the activities of the earth samples dehydrated to different extents showed that while the loss of the planar water increased the activity of the earth, the loss of crystal lattice water affected the activity adversely.

These results gave an insight into the mechanism of the activation of the earth by the various processes studied.

In activation of the earth by electrolysis and electrodialysis the hydrogen derived from water replaces the various bases which are extracted at the cathode in the form of hydroxides.

In activation by acids, the action of acid results in reducing the earth to the fundamental montmorillonite structures, replacing the bases by hydrogen and opening the crystal channels by dissolving the adhering impurities. This facilitates zeolitic exchange of hydrogen when treated with salt solutions.

In acid activation the nature of the anion in the acid employed has thus no influence. The difference in activation, brought about by hydrochloric acid on one hand and sulphuric acid on the other, is due to the insolubility of calcium sulphate, the deposition of which clogs the crystal channel and thus lessens the exchange capacity of the earth.

That an activated earth behaves as a hydrogen zeolite is further shown by the fact that the hydrogen can be progressively replaced by using higher and higher concentrations of a replacing cation. Accurate measurements by conductivity method of the hydrogen ion so extracted showed that the replacement proceeds according to the law of mass action:

$$K = \frac{[H]^2}{[\square \cdot H - H^+][Na^+ - H^+]},$$

where  $\square \cdot H$  denotes the earth complex.

The low value of the equilibrium ( $K$ ) found indicated that the hydrogen is tenaciously held to the surface. This observation is in conformity with the peculiar behaviour of hydrogen in hydrogen clays found by Wegner and Jenny.<sup>4</sup>

It has long been advocated by Eckart<sup>5</sup> and also by Welde<sup>6</sup> that the increased activity of the earth on acid treatment is due to the dissolution of alumina and silica from the body of the earth resulting in an increased porosity and absorption. The increased porosity cannot, however, explain the direct dependence of activity exclusively on the hydrogen zeolitic content of the earth. In the light of the above results the increased activity is to be attributed to the removal of most of the extraneous matter from the earth and to the opening of the crystal channels, making the exchangeable hydrogen available for reaction. Prolonged digestion with acid impairs the activity because it results in the decomposition of the montmorillonite structures. The results obtained in the present paper are in support of this view.

For the manufacture of activated fuller's earth, the following processes have been tried: (1) simple roasting (calcining), (2) digestion in acid solutions, or in mixture of acid solutions and salts, (3) digestion in alkalis; (4) subjecting the dry earths to gaseous acids, and (5) electrolysis and electrodialysis of aqueous suspensions. The suitability of any of the above processes for adoption on a commercial basis is governed by the nature of the raw material. So far as most of the common earths and, particularly, Indian earths are concerned, the processes 1, 4 and 5 are unsuitable, as, either they yield unactivated or only weakly activated products or the cost of their operation is forbidding. In acid activation, nitric, oxalic and sulphurous acids are unsuitable. For Indian earths, only sulphuric and hydrochloric acid solutions have been found to give promising results as the activating agents. The optimum conditions of operation with regard to each of the two reagents have been determined in the present investigation.

Although deposits of fuller's earth are spread all over India, a commercially workable supply is obtainable only at a few deposits. The following table shows the output of fuller's earth in India from 1933 to 1937.—

	1933 Tons	1934 Tons	1935 Tons	1936 Tons	1937 Tons
Hyderabad (Sind)	688	821	685	879	
Khairpur State	3,776	4,281	4,201	2,928	4,844
Bikaner	1,491	2,213	1,437	1,514	869
Jaisalmer	17	18	17	17	13
Jodhpur	1,250	1,168	1,260	1,251	1,640

In the present research we have used the earth from Hyderabad (Sind)

#### EXPERIMENTAL.

(I) Activation with hydrochloric and sulphuric acid solutions: The method of activation consisted in heating under reflux a weighed quantity of earth

with a measured volume of acid solution of a known strength. After digestion for about three hours, the mixture was filtered through a buchner. The earth was washed free from acid, dried at  $110^{\circ}$  before testing for activity. The volume of the acid solution used was such as to sufficiently cover the earth in the digestion flask. The proportion of the volume of the acid solution to the quantity of the earth was 200 c.c. of acid solution/100 gms. of earth. The decolorising experiments were carried out on a sample of safflower oil, the original colour of which was 9.8 yellow Lovibond units, using 1% earth. The following table gives the results:—

*Hydrochloric acid*

Acid strength	Loss of earth in activation %	Units of Lovibond colour removed
1N	12.0	7.1
3N	20.1	7.5
5N	27.7	8.5
7N	32.4	4.4

*Sulphuric acid*

Acid strength	Loss of earth in activation %	Units of Lovibond colour removed
1N	11.5	6.9
3N	18.0	7.4
5N	23.5	8.4
7N	25.7	7.4

It will be seen that the activity of the earth obtained is highest at 5N acid strength, and drops below and above that strength. The earth, however, suffers progressive loss in weight with the acid strength indicating that with higher concentration of acid solutions more decomposition of the earth takes place with loss in activity.

The action of sulphuric acid is consistently of lower order than that of hydrochloric acid. Here also highest activity is obtained at 5N acid concentration.

(II) Activation with mixtures of sulphuric and hydrochloric acids was carried out and the activity of the product determined. The acids were mixed in equal proportions to give the suitable strengths. The following table gives the activity of the treated earths:—

*Acid mixtures*

Total strength of the acids.	Units of Lovibond colour removed
3N	7.5
5N	7.4
7N	6.2

The activity of the product is lower than that obtained with a single acid. Mixtures of acids in various other proportions were tried but all gave lower activity than the product obtained with 5N sulphuric acid

(III) Activation of the earth was tried with sulphuric acid solution to which an equivalent amount of sodium chloride was added. The following results were obtained .—

Acid strength	Lovibond units of colour removed
3N	7.2
5N	7.4
7N	6.2

Here the activity obtained is almost the same as with the mixture of acids

(IV) *Dry Process* —In this method a thick paste was formed by grinding with the powdered earth a requisite volume of concentrated sulphuric acid. The paste was heated in a porcelain basin on a sandbath for about two hours at 150°C. The dry product in the basin was powdered and washed free from acid and dried. The following table gives the results —

H <sub>2</sub> SO <sub>4</sub> per 100 gms of earth	Equivalent Normality in the wet method	Loss of earth on activation %	Unit of Lovibond colour removed
10	1.02	7.5	7.2
20	2.04	10.6	8.4
30	3.06	12.4	8.3
40	4.08	15.6	7.0
50	5.10	17.7	5.4
60	6.12	20.5	3.9
70	7.14	21.4	2.3
80	8.16	22.6	1.8
90	9.18	23.7	1.6

There was no free acid in the filtrate. The results show that highest activity is obtained with 20 to 30% sulphuric acid. In the wet process this acid quantity would amount to 2.04N and 3.06N and gives a product the activity of which is as much as that obtained with 5N sulphuric acid solution in the wet process. If the activation is carried at about 200°C, the activity is found to decrease and the iron salts decompose into insoluble iron oxide which colours the final product.

It is intended to try this process on a semi-commercial stage.

### SUMMARY

A review of previous work of the authors on the activation and clarifying action of fuller's earth is given.

A dry process of activation which consists of heating a mixture of the raw earth with 20% of sulphuric acid at 150°C gives a satisfactory product.

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## ON THE UTILISATION OF INDIAN RAW MATERIALS FOR THE MANUFACTURE OF SULPHURIC ACID

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*(Read at Symposium, April 19, 1941)*

Sulphuric acid is one of the most important of all chemicals, because of the wide use of the acid in many different industrial works. It is to the chemical industry what iron is to metallurgy. The general public, however, do not realise this fact, for sulphuric acid does not appear in the finished product as does iron or steel, but is only an intermediate raw material essential in many industries, such as, for example, the manufacture of phosphatic fertilisers, munitions and explosives, dyes, petroleum products, of various acids and innumerable other chemical and metallurgical products. The demand for sulphuric acid responds much more quickly to a general slump or boom in the industrial world than does the demand for iron or steel, so that it can rightly be said that the demand for this acid for chemical and metallurgical industries is an accurate and sensitive barometer for the general business conditions.

In India the principal manufacturers are the coal, iron and steel companies situated in Bengal, Bihar and Orissa, the ammunition factories and the chemical companies (D. Waldie & Co., with works at Konnagar and Cawnpore, the Bengal Chemical & Pharmaceutical Works, Ltd. of Calcutta (established 1909), Messrs Parry & Co. of Ranipet (established 1909), the Eastern Chemical Co. with works at Bombay (established 1913), Dharmji Morariji & Co. of Bombay, the Baroda Chemical Works, Baroda). The entire manufacture of sulphuric acid in India is based on imported sulphur.

### *Sulphuric Acid from Sulphate Minerals*

One of the most widespread and easily obtainable sources of sulphur is gypsum or anhydrite and the urge towards national self-sufficiency in sulphur is causing considerable attention to be paid to the problem of the utilisation of calcium sulphate, particularly in Russia and France. The Committee appointed by the French Government in August 1937 had recommended (in view of the difficulty of importing adequate supplies of pyrites from Spain) that a large-scale industry should be established for the manufacture of sulphuric acid from gypsum. An extensive report of laboratory and factory scale investigation of a process has been made by the Russian investigators S. M. Rojak, M. I. Gerselman, K. F. Miloslavski and Z. I. Nagerova (*Trans. All Union Sci. Inst. Cement*, 1935, No. 10, 5). It is said that a suitable composition for the raw mixture is calcium sulphate 80%, dried clay 15%, and coke, anthracite,

etc 5% A microscopic study of the clinker shows that the petrographic structure is identical with that of ordinary Portland cement, provided the burning is correctly carried out A somewhat similar process has been investigated by V S Dubey, M B Rane and M Kanakarathnam (*Bull. Indian Ind Res Bureau*, 1937, No 6) in which alumina and sulphur dioxide are produced from bauxite gypsum mixtures No carbon was added to aid displacement of  $\text{SO}_2$  from gypsum If the mixture of bauxite and gypsum in the ratio of 2 : 5 are heated at  $1200\text{--}1250^\circ$  for six to seven hours, the sulphur dioxide is expelled completely from gypsum The resulting calcium aluminates on hydrolysis furnish pure alumina

The first published description of the process as employed by Imperial Chemical Industries, Ltd, at Billingham to manufacture high class Portland cement and sulphuric acid from anhydrite and white clay was made by M Nicoléts (*XVII Cong Chim Ind Paris*)

P P Budnikov and E I Kretsch (*J Appl Chem Russ*, 1936, 9, 1929) have studied the reaction between finely ground calcium sulphate and carbon at  $800\text{--}1200^\circ$  The rate of reduction is proportional to the relative concentration of carbon and inversely proportional to the diameter of the particles The same authors (*ibid*, 995) find that the direct decomposition of calcium sulphate by chlorine at  $900\text{--}950^\circ$  is accelerated by the addition of various substances, nickelous sulphate having the greatest effect. It is stated that a 100% yield of  $\text{SO}_2$  was obtained at  $1100\text{--}1150^\circ$  and 86.5% yield at  $1000\text{--}1050^\circ$  in the presence of silica In this projected process the chlorine is recovered as hydrochloric acid.

The reaction between pure calcium sulphate and kaolin was studied by G Marchel (*J Chem Phys*, 1926, 23, 38–60) and the thermal dissociation in the presence of oxides of iron, silicon, aluminium and chromium has been studied by the Russian chemists (of *J Appl Chem Russ*, 1932, 5, 897–901)

India is quite rich in deposits of high grade gypsum Most of the gypsum now mined is being used in the cement industry, where gypsum is added to the ground cement clinker to control the setting properties of the cement The production of gypsum is increasing as the following statistics show:—

Period	Average annual production
1914–18	18,857 tons
1919–23	35,133 „
1924–28	41,199 „
1929–33	50,112 „

70% comes from the Punjab, the remainder from Kashmir, Rajputana and Madras In the Jhelum district of the Punjab the mineral occurs in enormous quantities and extends through Shahpur and Mianwali districts along the whole length of the southern flank of the range from Jalalpur to Kalabagh on the Indus At Khewra in the Jhelum district, the Department of Northern

India Salt Revenue undertake the quarrying of gypsum as a subsidiary industry.

Immense deposits also exist in the trans-Indus salt region of the Kohat district, North-West Frontier Province, where more or less continuous masses up to 200 ft in thickness are found with bands of shale and clay. Huge deposits also occur in Spiti and Kanaur, in the Punjab Himalayas.

The Kashmir deposits are also immense and are stretched for fifteen miles to the north of the Jhelum valley cart road near Braupara in the Uri Tehsil.

In Rajputana, the Bikaner State accounts for 54% of the production, the Jodhpur State for 45% and the Jaisalmer State for the rest.

In Southern India gypsum is widely distributed in the cretaceous rocks of the Trichinopoly district. The mineral is mined at Karai in the Perambalur Taluq and at Ottathur in the same Taluq and at Maravathur in Udaiyarpalayam Taluq.

In his evidence before the Indian Tariff Board on Heavy Chemical Industry (1930, Vol II, p 481) Sir Edwin Pascoe stated that gypsum of a very superior quality occurs in immense quantities in Burma, and can be picked up by hand labour over large areas of the country.

Another mineral which has a promising future in India is barytes, the sulphate of barium, a heavy white mineral which finds its chief application at present in the paint industry. India has very rich deposits of this mineral. The largest deposits occur in the Madras Presidency. Mining was started in 1918 at Betumcherla in Kurnool district and over 24,500 tons had been exported from this district by the end of 1931. As a result of systematic investigation in 1932, Mr A. L. Coulson listed sixty localities in this region.

District.	Taluq	No. of places
Cuddapah	Pulivendla	8
Cuddapah	Other Taluqs	5
Anantapur	Tadpatri	8
Anantapur	Other Taluqs	3
Kurnool	Dhone	20
Kurnool	Other Taluqs	7

According to the estimate of Mr A. L. Coulson (*Mem Geol Surv Ind*, LXIV, Pt 1, 1933) at Kottapalle in the Pulivendla Taluq of the Cuddapah district there are over 30,000 tons of barytes in the first 20 ft of depth. The Mutesukota deposit may contain 75,000 tons. Four veins have been found near Nerijampuralle in Anantapur the largest of which is from 3 to 11 ft wide and has been traced for more than half a mile along its strike.

Barytes has been mined in the Alwar State of Rajputana since 1921, the total output up to the end of 1932 being 14,302 tons. There are four separate deposits, the most important being situated four miles north by east of Parisal, where a vein of pure white mineral has been got.

It will thus be seen that we have extensive deposits of barytes in India, and it will be worth the while to examine the possibilities of obtaining sulphuric acid from this mineral. According to a patent granted to Mr M Kanakaratnam, sulphur dioxide is completely expelled by heating mixtures of bauxite and barytes in suitable proportions. The Brown Co patented a process (U S P 2,205,929) in which sulphuric acid and caustic soda are produced from barium sulphate and sodium sulphate as raw materials. Barium sulphate is reduced by carbon to barium sulphide which is treated with aqueous sodium sulphate to give a solution of sodium sulphide. This is then causticised with cupric oxide, using a method similar to that employed by Boguslovski and his co-workers.

It has been reported that sulphur in considerable quantity can be had from Baluchistan and that pyrites occur in the Simla Hills and in the province of Bihar. Detailed information about these deposits is not, however, available, the possibility of recovery of sulphur from well-known sulphate deposits cannot therefore be ruled out of consideration.

## HEAVY CHEMICAL INDUSTRIES

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(Read at Symposium, April 19, 1941)

India's industrial development took a sharp turn during the last war. The growth of various post-war industries caused a marked decline in the import of certain classes of finished articles, e.g. soap, rubber goods, pottery, paint, etc. But while the import of manufactured goods have shown a steady and marked decline, there are two important categories in which there has been a phenomenal increase. These two categories are machineries and chemicals. The gap in the industrial structure of the country to which much attention has recently been given both in the press and in public primarily concerns *machineries and chemicals*. Rectification of this deficiency in the industrial equipment of the country can to a great extent be achieved with the development of (1) *the Metallurgical Industry*, and of (2) *the Basic Chemical Industry*. In fact a co-ordinated scheme of development of these two industries should be taken up simultaneously.

Heavy chemicals, as usually classified, include amongst others the following —

Acids, alkalis both caustic and carbonated and salts, e.g. ammonium sulphate, sodium sulphate, sulphides, hydrosulphites, hypo-sulphites, sodium silicate and bichromate, magnesium, zinc and lead compounds, copper sulphate and calcium carbide.

**Acids** — It is well known that for the development of Indian chemical industries there should be cheap and abundant supply of  $H_2SO_4$ . As the manufacture of this acid depends on the supply of sulphur or pyrites, a survey of such sources is the first step to be undertaken. Acid made in India from imported sulphur can neither be cheap nor abundant. The activities of the Board of Scientific and Industrial Research have, within the short time of its existence, been very encouraging in this direction. They are enumerated below:

- 1 Possibilities of mining sulphur were indicated in the Survey Report of the Geological Survey in Sind and Baluchistan and attempts are being made to exploit it.
- 2 The recovery of sulphur from benzol by the two important factories at Jamshedpur and Bararee are going to be attended to.
- 3 Particular attention is being drawn to the  $SO_2$  set free during metallurgical operations involving the use of pyrites particularly during the manufacture of copper and zinc as it is considered as a rich and potential source of the acid.
- 4 Sulphur from coal and oil are being examined for utility in trade.

In my opinion the source of  $\text{SO}_2$  supply from the metallurgical operations need urgent and prompt attention *The dilution of  $\text{SO}_2$  set free in the manufacture of copper may be an apparent hindrance but intensive research may help to improve the methods of manufacture and evolve a method of utilising the waste  $\text{SO}_2$  gas*

Sulphuric acid is cheap in Europe but owing to its corrosive quality and high freight this industry in India has enjoyed a natural protection But its restricted output and high cost raises the cost of the manufacture of materials derived from this basic chemical The foreign manufacturers have taken full advantage of this situation as the import value of salts derived from this acid mounts up to a respectable figure

**Alkalis**—The other important heavy basic chemicals which require our attention is the manufacture of alkalis, both caustic and carbonated The value of import of alkali and their products easily derived from it exceeds a third of the value of the total chemicals imported into this country It is natural therefore that the enterprising firms of the Tatas and I C I decided to start manufacture of this important basic material in this country The Mettur Industrial and Chemical Corporation are, I understand, also in the field for the manufacture of caustic soda and bleaching powder The I C I. factory in Bengal is now producing caustic liquor and hypo-chlorite solution which finds a ready market in that part of the country A good portion of the requirements of bleaching powder and caustic alkali is going to be met from these newly developed sources

The manufacture of the *carbonated alkali* (soda ash) need not be confined to the electrolytic process In places where the raw materials for the electrolytic process are not easily available but where plenty of ammonia may be made available, synthetically or otherwise, the possibilities of the new process in which liquid ammonia is used as solvent may well be investigated. Japan, Russia and Germany have by different modifications of this process, the underlying theoretical principle being the same, started on soda ash manufacture on a commercial scale

**Calcium carbide**—The question of supply of ammonia suggests the possibilities of the carbide industry in this country But the claim of this industry is supreme from the point of view of a country's safety, well-being and prosperity As a source of acetic acid and acetone it has its utility in industries connected with (1) artificial silk, (2) plastics and rubber, (3) varnishes and pigments (lead), (4) dyestuff and perfumes, (5) explosives, (6) artificial leather, and (7) pharmaceutical products The use of cyanamide as a fertiliser cannot be too strongly recommended in a predominantly agricultural country such as ours It is true that a certain amount of some of these products are being obtained in this country by wood distillation and the possibility of preparing acetone by fermentation and as a by-product of the petroleum industry are being actively investigated, but students of chemistry are well aware that synthetic acetic acid, acetate of lime and acetone obtained from

acetylene are fast appropriating the place occupied by the same products obtained by the foregoing processes

It is, therefore, necessary that where cheap power and good lime are available a carbide plant should be installed. Between Bihar and Bengal, in regions near the coalfields there are good lime quarries. The next suitable place for a carbide plant will be Madras where hydro-electric power is cheap. Here, if the coal supply is not so abundant, plenty of charcoal is available at a cheap price. And there already exists a large market for this commodity at both the places. It has been estimated that on a rough estimate the cost of production will be somewhere about Rs 230 per ton while its pre-war price was quoted at Rs 430 per ton. The economic unit will be a plant of five ton capacity.

*Alumina and aluminium* —In view of the growing importance of aluminium, the new French process (Seailles) of treating bauxite for alumina is worth notice. Limestone and bauxite are calcined at a temperature of 950–1,100°C. The crude aluminate of calcium is treated with water on the counter current principle under controlled conditions and the resulting solution of calcium aluminate is filtered and immediately treated with carbon dioxide obtained from the first calcination, a mixture of anhydrous alumina and calcium carbonate being produced. The final separation of anhydrous alumina from calcium carbonate can be brought about by treating a suspension of the mixture with water saturated with carbon dioxide when the bicarbonate of calcium formed goes into solution leaving anhydrous alumina behind. In view of an ample supply of bauxite in this country, this process has much to commend for production of aluminium.



## SOME OBSERVATIONS ON THE HEAVY CHEMICAL INDUSTRIES OF INDIA

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*(Read at Symposium, April 19, 1941)*

A discussion on heavy chemical industry immediately brings in the question of sulphuric acid. It is often said, and very rightly indeed, that the industrial development of a country is measured by the quantity of sulphuric acid it consumes. The subject of sulphuric acid again brings in the problem of sulphur of which there is no appreciable source in this country. India, like many other countries, has to depend upon imported sulphur. From the amount of sulphuric acid produced in different centres an amount of the sulphur consumed may be judged.

Centre	Production of sulphuric acid in tons per day.
Amritsar	10
Jamshedpur	50
Cawnpore	10
Bombay	5
Madras	5
Mysore	30
Calcutta	45
TOTAL	160 tons

Taking the sulphur content about 33%, daily consumption of sulphur is about 50 tons. Previous to the war the main source of supply of sulphur was Sicily, on account of the Sicilian sulphur being free from arsenic. But since the outbreak of the present war America has become our main source of sulphur. But the shipments are so irregular that at any time there can be a crisis in the manufacture of sulphuric acid. A source of sulphur has recently been found in Baluchistan, which was in fact known long ago. It can be worked out now and the Government of India have already taken up the work in hand. But transport difficulty and other consideration stand in the way of its economic exploitation at the present moment.

There are, however, good deposits of pyrites and gypsum in India which contain a fair proportion of sulphur. But all the sulphuric acid plants in India are equipped with sulphur burners.

Industry in this country sprang up and developed at the natural instinct of some of the great men of the country. There was no national planning of industries. Countries, where industries have been set up on national plannings, are not threatened to-day with such a crisis. Their big industries are planned

on local advantageous circumstances Manufacture of sulphuric acid from pyrites is being carried out in many countries Gypsum seems to have attracted lesser attention, yet a major portion of the U S S R acids are known to be produced from this source to suit their local conditions

It must be admitted on all facts that the individual manufacturers in this country are now busy beyond their normal capacities It is, therefore, in our opinion, one of the foremost duties of the Board of Industrial and Scientific Research to work out and set up a pilot plant for sulphuric acid manufacture from pyrites and gypsum after having explored the possibilities of all raw materials, specially of gypsum and pyrites, and this will be of great help to the manufacturers

There is, however, one difficulty with regard to the use of Indian pyrites As far as we know, there is hardly any deposit free from arsenic Gypsum, however, is quite pure and may serve as a supplement for the manufacture of acids used for medicinal or other purposes of human consumption

There are some who hint at the inefficiency of Indian manufacturers and outcise adversely the protective measures under which they are working If a foreign manufacturer can produce and export a commodity at lower price, it is, in their opinion, unreasonable to ask for any protection after the expiry of a long period of spoon feeding and thereby indirectly taxing the poor rate-payers While their reasonings are perfectly sound, their analysis of the situation is, however, hardly correct The manufacturers are neither deriving a high profit nor are their production efficiency low It is the great handicap under which they work which makes the price of their goods higher than expected

In the first instance the raw materials are to be brought from a very great distance Railway freight naturally is very high—in some cases two to three times the price of the stuff itself An interesting instance on this point might be cited here. A few years back, the railway freight of bauxite to Howrah Station was double that at the jetty It was in the interest of Government to get a cheap export, so the freight by steamer had been reduced to the lowest limit But to ask for such help in case of the poor Indian manufacturer will bring in the paraphernalia of Committee, Commission and similar dilatory tactics and ultimate shelving of the question itself.

Secondly, we find exorbitant freights charged on acids for their inland transport Due mainly to this reason, heavy chemical industries are all situated near about big metropolis where the cost of labour and taxation are extremely high. Had such factories been distributed all over the country, consumers would have been saved the cost of transport which, again, is not a negligible factor of the price of cheap domestic articles like alum, mag sulph, ferri sulph., etc. In this connection we should consider another possible danger that is lurking in the horizon If Calcutta is subjected to an air raid similar to that of London, all Indian industries will cease to function in a day. It is

high time for the Government to think in this line and consider what steps should be taken to transfer some of the key industries deeper into the country

In spite of the difficulties enumerated above, perhaps a time has come when we should look forward. India has got huge deposits of bauxite, chromite, magnesite, pyrolusite and many other rich ores. We have copper, iron, lead and other metals. Our coal resource is not low. What difficulties we have are all artificially created and can be brushed off with united efforts.

We should try to reduce as far as possible the free exports of the valuable ores. If they are to be exported, they must go out as finished stuff. It is high time that the manufacturers in the line put their heads together and devise means for it.

While we find good strides have been made in the production of heavy chemicals after the last Great War, the problem of potash industry still remains unsolved. India is entirely dependent for her supply of potash and soda on foreign imports though we have well-established industries for the salts of aluminium, zinc, copper, lead and iron. Chromium industry also is rapidly being extended and there are several firms seriously working with manganese compounds.

Before the outbreak of war, most of the potassium salts were imported from Germany, Holland and France. At present America has captured the market, though its potash resource is not a very big one. Prices, therefore, have gone up enormously as is evident from the following schedule —

Items	Pre war Price	Present Price.
Potassium Carbonate	Rs 21 per cwt	Rs 60 per cwt
„ Bicarbonate	Rs 20 „ „	Rs 86 „ „
„ Bichromate	Rs 36 „ „	Rs 104 „ „
„ Ferrocyanide	Rs 68 „ „	Rs 400 „ „
„ Sulphate	Rs 7 „ „	Rs 15 „ „
„ Cyanide	Rs 1.4-0 „ lb	Rs 2.8 0 „ lb
„ Caustic	Rs 27 „ cwt.	Rs 70 „ cwt

Even before the war, prices of potassium salts were comparatively higher. A consideration of this fact prompted the reduction of import duty from 30 to 25%. The plight of the consumers at the present market can, therefore, be easily imagined.

Wood ash was the only starting material for potassium salts, even up to the closing years of the nineteenth century. Great forests of the U.S.A., Canada and Russia have dwindled, yielding its potassium throughout the whole world. Gradually, however, the molasses from beet sugar has taken up its place, from which source France, Belgium and Holland produce a very large quantity of potassium compounds. In Germany, an additional source is utilised, that is the great Staassfurt Deposit. Though the residue left after the fermentation of this molass is rich in potassium salts, the preparation of potassium carbonate from it entails a very lengthy process. The composition

of the calcined stuff from molass will give an idea of the extent of impurities to be removed It contains —

	1	2	3
Potash	51 72%	47 67%	50 38%
Soda	8 „	11 43 „	8 29 „
Lime	5 04 „	3 6 „	3 12 „
Magnesia	18 „	10 „	18 „
Carbonic Acid	28 9 „	27 04 „	28 7 „

The remainder consists of phosphoric and silicic acids, chlorine, oxides of iron, etc, amounting 10 to 20% Nor is the manufacture from pot chloride of Stassfurt less elaborate, since the simple ammonia process is not suited for it. If the countries mentioned above control the potassium market of the world, it is only because of their initial start and the large production they command.

Forest is a natural resource of India. Excepting perhaps Bengal and Bihar, wood is used as fuel all throughout for domestic purpose. Even factory power in tea-gardens and industry situated in the interior of the country is obtained from wood fire. In Southern India groundnut mills are run by burning the husks. These ashes are fairly rich in potassium carbonate. While it may be difficult, if not impossible, to gather the domestic wood ash, those from industrial centres are easily procurable. Usually they are run to waste. So a very small price will suffice to attract them.

With the growth of the importance and consumption of power alcohol, fermentation industries are coming more into the field. Recent U.P. move for the compulsory utilisation of power alcohol has given a great impetus. It is, therefore, expected that the molass-residue left after fermentation will attract greater attention for its utilisation. Considering the cheap fuel-value, particularly in Bengal, this valuable by-product is worth evaporation and calcination, whereby at least a good concentrated potass manure may be obtained. A sample of such a liquor on evaporation and calcination yield a product differing from the foreign ash only in having a large percentage of sulphates.

But potassium is found in a more concentrated form in the Punjab, the U.P. and North Bihar as nitrate. It appears on ground as an efflorescence which is collected and sold as such by cultivators. There are purifying factories who produce an almost pure salt by simple crystallisation.

Unfortunately we have no statistics at hand to show what amount of nitrate is annually produced. But from our experience of Calcutta market, we know shiploads of this nitre are exported every month to Java, China, Japan, Hongkong and Australia. Naturally, there exist all facilities for chief transports to port and there being no restriction or duty, export is very easy. It is not known what price the original substance brings to the cultivators; but after several transference of hands Calcutta price ranges from Rs 12 to Rs 13 per cwt for a variety of 99% purity. Price for lesser purity are much lower. For instance, a 90% variety can easily be bought at Rs.10

per cwt These prices are all of the present market which before war was about 33 to 50% lower It is the general impression that these exports are meant for manurial purpose Being a combined potassium and nitrogen source, perhaps it is true for consignments to Java and similar cane-producing countries But considering the stress given by exporters on quality this explanation seems untenable An industrial utilisation can reasonably be suspected

In this connection, one curious fact needs some comment When taxations are heavily levied directly and indirectly on already over-burdened rate-payers, it is a mystery why such an important item like nitre may be allowed to be exported free It may be argued that such a duty may prove detrimental by the increase in price and inhibit the existing business But considering the fact that nitre market is never a fixed one and is subject more or less to the whim of middleman in Calcutta, an addition of 10 to 15% of export duty is hardly expected to be of any untoward effect Moreover this charge will either fall on the foreign purchaser or be borne by exporting houses Stoppage of the Norwegian and German synthetic soda nitre has greatly increased the demand of Indian nitre Whole of this benefit is being enjoyed by middleman, actual producers remaining ignorant of it Money obtained from this source may be utilised for their benefit, for the betterment of the cultivation as a whole, like jute in Bengal

Nitre is an excellent starting material for the preparation of all potassium salts Mixed with charcoal or half-dry molasses it burns well with a good heat efficiency The ash left behind is almost pure carbonate An average composition is as follows —

$K_2CO_3$	95%
$Na_2CO_3$	nil
Unburnt carbon	2%
$KNO_2$	1%
$KNO_3$	nil
Sulphide and silicate	trace

This can be transformed into caustic if mixed with lime, at the time of combustion Dichromates and sulphates may be obtained by double decomposition with the respective sodium salts

A very important factor for the commercial success of potassium industry is the purity of potassium nitrate readily obtained in the market It requires practically no big installation or plant to prepare potassium carbonate, caustic or sulphate Ferrocyanide and cyanides would require a reverberatory furnace. Costs of production obtained from our experimental trials as shown below are not very high

Items.	Pre-war import costs	Manufactured costs based on pre-war nitre price
Potassium Carbonate	Rs 21 per cwt	Rs 20 per cwt
Caustic Potash	Rs 27 .. ..	Rs 26 .. ..
Potassium Sulphate	Rs 7 .. ..	Rs 7 .. ..
„ Dichromate	Rs 36 .. ..	We have not yet come to a definite figure

They come very near to the wholesale import price of the foreign materials. With better experience, these are expected to go lower down, and there is no reason why we should not be able to normally compete with the importer. We have not yet arrived at any figure for ferrocyanides and cyanides, but since the raw materials for these are very cheap, there is no reason why their economic aspects should be less optimistic. Yet, it must be clearly stated, it will be impossible to bring such an industry to a successful end without the help and active co-operation of the Government. It may be necessary to protect it by a special tariff till the stage of infancy is passed.

# SCOPE FOR THE MANUFACTURE OF SULPHURIC ACID AND HEAVY CHEMICALS BASED ON IT IN HYDERABAD

By M. QURESHI

(Read at Symposium, April 19, 1941)

'We may judge with great accuracy the commercial prosperity of a country from the amount of sulphuric acid it consumes' This is as much true to-day as it was in 1840, a century ago, when Liebig wrote this sentence. Judged from this standard, India is very poor compared to other countries. The world output of sulphuric acid in 1937 was about 10 million tons per annum of which Britain's share was nearly 1 million tons. India's present output of this chemical can be roughly estimated at about 40,000 tons, or nearly one-twentyfifth of that of Great Britain. The total consumption of this chemical in India is not very much different from this figure, as the quantity imported from other countries (representing pure and analytical reagent qualities) does not exceed 300 tons per annum.

Sulphuric acid is the parent substance of modern chemical industry. It is the starting point in the manufacture of many heavy chemicals, such as hydrochloric acid, nitric acid, aluminium sulphate, alum, ammonium sulphate, superphosphate of calcium, sodium sulphate, ferrous sulphate, etc., which are used in large quantities by other industries. It is no less essential to the manufacture of fine chemicals and dye-stuffs. Many of the largest industries which are of vital importance to us in peace and war, such as the manufacture of fertilisers, explosives, dyes, metallurgy, petroleum-refining and electroplating—to mention only a few out of a long list—depend upon sulphuric acid or other chemicals prepared with the help of this acid. As the acid itself is highly corrosive and is subject to heavy freight charges, only a small portion of its immense output comes on the market. A large portion is used by its manufacturers in producing other heavy chemicals on the spot. Big industries, consuming large quantities, make their own acid. The growth of industry in India is, thus, intimately connected with the increase in the production of this important chemical. Each new industrial enterprise will demand more sulphuric acid, and vice versa an increase in sulphuric acid production will mean more industrial expansion. It is, therefore, highly important that at this stage of our country's industrial progress we should take a stock of our country's resources with regard to the production of this vital necessity.

The raw materials for the production of sulphuric acid that come into serious consideration are brimstone or native sulphur and iron pyrites, although zincblende, copper pyrites, galena, gypsum and sulphur dioxide produced in metallurgical processes have also been used to a limited extent in some

countries In India sulphuric acid has so far been manufactured mainly from native sulphur imported from Sicily, Japan and the United States of America. The war has cut down supplies from Sicily and Japan and the Indian manufacturer has to rely on the American supply, for which he pays about Rs 130 per ton at port, the pre-war price being about Rs 70 per ton. It need not be too much stressed that, unless India possesses extensive and cheap sources of sulphur within her own borders, she cannot hope to build up a chemical industry on an economical and permanent footing. During recent years, search for sources of sulphur has led to the discovery of iron pyrites in two places, namely Simla and Tandur collieries (Hyderabad-Dn). The deposits near Simla, which are stated to be quite extensive, have been developed by Dr Kedar Nath of Delhi who holds a lease for the mines. In Hyderabad, the pyrites occurs in thin layers, interbedded in the coal seams at Tandur collieries. The amount available at present is not more than 60 tons a month, but the quantity will increase with the output of coal which, in turn, is bound to increase with the expansion of industries in the State. Native sulphur has, so far, been found in Baluchistan and Simla Hills. The Baluchistan deposits are perhaps too far away from the existing centres of sulphuric acid industry to be of economic value to them at present, but, with the development of communications and the spirit of industrial enterprise in the country, these deposits might prove a very useful asset in future. The Simla deposits, on the other hand, can immediately serve as a source of economic supply to the sulphuric acid industry. If these expectations are realised, India will be able to manufacture sulphuric acid and other heavy chemicals cheaply and in quantities sufficient to meet the demands of her growing industries.

The development of industry and agriculture in H E H the Nizam's Dominions during the last decade has led to an increasing demand for heavy chemicals, as testified by the import figures for the last five years, given below —

*Import of some heavy chemicals into Hyderabad.*

Commodity	Approximate quantity in tons				
	1936	1937	1938	1939	1940
Sulphuric acid	180	65	77	103	103
Hydrochloric acid	121	104	129	136	109
Nitric acid	54	34	46	62	89
Alum	41	59	57	146	109
Chemical manures (including ammonia sulphate and superphosphate)	300	255	300	1,260	1,640
Caustic soda	115	148	184	212	278

The figures for other heavy chemicals based on sulphuric acid are not available separately, but information gathered from Customs' authorities and

industrial concerns shows that the import of superphosphate of lime, ammonium sulphate, aluminum sulphate, magnesium sulphate, magnesium chloride, sodium sulphate and ferrous sulphate into the State is steadily increasing. The establishment of cane sugar industry and development of agriculture and fruit cultivation have increased the demand for fertilisers. The demand for heavy chemicals, already consumed in fairly large quantities by the existing textile industry, is bound to increase through the establishment of new industries such as the manufacture of paper, iron and steel industry and leather manufacture. The paper mills are expected to begin work shortly, while the manufacture of iron and steel is receiving serious consideration. The stage has, thus, been reached in the industrial progress of Hyderabad when the manufacture of sulphuric acid and heavy chemicals based on it could be economically and profitably taken up in the State. For some time past, Messrs Vazir Sultan & Sons, Hyderabad, have been preparing commercial sulphuric acid and nitric acid from imported brimstone by the chamber method. But the scale of their operation is limited and no attempt has been made to prepare other heavy chemicals. Taking into consideration the figures for the consumption of sulphuric acid and heavy chemicals based on it, in the State, it has been estimated that a chamber plant, producing 4 tons of sulphuric acid per day, will meet the existing requirements of the State in these chemicals. The cost of the whole plant for the manufacture of sulphuric acid and other heavy chemicals, mentioned above, including a chamber plant with a maximum capacity of 6 tons, machinery and building, is estimated roughly at Rs 6 lacs, and the working capital at about Rs 1 lac. The main source of sulphur dioxide in this plant will be the local pyrites, but some imported brimstone may also be used until such time as the output of the pyrites is enough to do without it. The pyrites found in the State has been thoroughly tested and found to be of a good quality, with a high percentage of sulphur and no arsenic. Its average chemical composition, along with that of the Simla pyrites and the ores found in other parts of the world, is given below —

*Composition of pyrites from various countries*

Pyrites	S	Fe	As	Cu	Pb	Zn	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Hyderabad coal pyrites	45.2	41.0	nil	nil	nil	nil	1.14	nil	2.06	3.17
Simla (reported by Dr Kedar Nath)	49.1	43.9	0.02	0.71	0.04		0.04		5.46	0.75
Spanish	48.5	40.9	0.33	4.21	1.52	0.22	0.9		3.46	
Portuguese	48.9	43.5	0.47	3.1	0.93	0.35	0.2		0.73	
French	46.4	39.0	0.1	1.5					9.25	3.75
West Phalian	45.6	38.5	trace		0.64	6			8.7	
Norwegian	49.0	42.3	nil	2.5	0.2	2.0	0.23	0.22	1.85	1.25
American coal pyrites	25.0	.								

The proper burning of iron pyrites for the production of sulphuric acid presents a serious difficulty. For the burning of lumps, ordinary burners of fire-place type with cast iron grate bars and brick walls are generally used. If these burners are designed and worked properly, the percentage of sulphur in the burnt pyrites should not exceed 1.2%. The sulphuric acid factory of the Mining & Chemical Industries Ltd., at Agra, is burning Simla pyrites with some success, and it is expected that with a little more improvement in their burners, the percentage of sulphur in the burnt pyrites will be reduced still further. For the burning of 'fines' which are necessarily formed in the process of mining and transporting the ore, automatic rotary shelf burners with horizontal shelves and air-cooled racking arms are being used in America and other countries. There is no reason why burners of this type could not be designed and constructed in this country.

## THE POTASH INDUSTRY IN INDIA

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(Read at Symposium, April 19, 1941)

Potassium salts are widely distributed in nature and in India the potential sources may be classified as follows —

- 1 (a) Lake brines  
(b) Sea-water  
(c) Underground brines  
(d) Swamp brines
- 2 Saline earths or efflorescences giving potassium nitrate and containing also potassium chloride and sulphate
- 3 Salt mines such as those at Khewra in the Salt Range and in Mandi State
- 4 Other minerals such as alunite ( $K_2SO_4$ ,  $Al_2(SO_4)_3$ ,  $4Al(OH)_3$ ), feldspar ( $K_2O$ ,  $Al_2O_3$ ,  $6SiO_2$ ), etc
- 5 Flue gases and cement kiln dust
- 6 Animal sources such as wool washings and sheep dung ash (kaino ash)
- 7 Vegetable sources, like molasses, bagasse, wood ashes and the ash of the water hyacinth which grows profusely in Bengal

Of all these sources of potassium only (1) and (2) appear to be of commercial importance in India in present circumstances

### *Mineral Sources*

A number of deposits containing potassium occur in the Salt Range in Northern India, though the quantity of these salts associated with the rock salt deposits is smaller than would be expected. The salts so far identified are sylvine or potassium chloride (KCl), langbeinite ( $K_2SO_4$ ,  $2MgSO_4$ ) and kainite ( $KCl$ ,  $MgSO_4$ ,  $3H_2O$ )

Dr. Warth discovered these deposits in the Mayo Salt Mine at Khewra in 1873. Dr W. A. K. Christie in his 'Notes on the Salt Deposits of the Cis-Indus Range' (*Rec. Geol. Surv. Ind.*, 1914, XLIV, 243) investigated the potassium-bearing salts of this mine and found that seams varied up to 7½' thick and averaged 6.8 to 9.6% potassium oxide in four seams and 14.4% potassium oxide in the case of a seam only about 2' thick. Later, Dr Murray Stuart in his article 'The Potash Salts of the Punjab Salt Range and Kohat' (*Rec. Geol. Surv. Ind.*, 1919, 28) reported on the saline deposits of Nurpur and

Warcha in the Salt Range and Kalabagh and Kohat in the trans-Indus region. He concluded that no continuous bed of potassium salts had been proved in these areas and expressed the opinion that it was unlikely that these salts would prove workable except possibly as a by-product during the normal course of mining for rock salt. In general, reports indicate that there are not workable quantities of salts at these places, but it has been suggested that these potential sources of potassium compounds should be re-investigated.

The other minerals contain potassium in very small quantities and no suggestion has yet been made to work them for potassium compounds.

### *Flue Gases and Cement Kiln Dust*

In Bulletin No. 42 of Indian Industries and Labour, it is stated that blast furnace dust contains potassium salts to a total content of 40–45% and that this source of potash is worth investigation. Further, it is claimed that, on account of the considerable amount of the iron ore smelted, it should be possible to produce potash from the flue dust at a steady rate which would go some way to meet the needs of agriculturists in India. This bulletin also states that the Katni Cement & Industrial Co. and the Jubbulpore Portland Cement Co. could produce 1 ton of potash per day, but the cost of production would be heavy.

In most cases, potassium salts present in the ore volatilise off. Whenever this does not happen, volatilisation is promoted by the addition of sodium chloride to the charge. In Britain, either electrical precipitation by Cottrell's method or a water spray process is used in the recovery of potash salts from these sources. In the cement kiln process, the gases leaving the kiln at 380° pass through a dust settling chamber where the temperature falls to 230° and thence to a spraying chamber. The liquid from the spraying chamber is filtered and evaporated to crystallise out the potash salts. The accumulation in the dust chamber is also leached with water and the solution similarly treated.

### *Animal Sources*

*Suint.* Wool washings containing wool fat or suint are evaporated to dryness and ignited, potassium carbonate being extracted from the residue by lixiviation with water. The composition of the salt obtained is as follows:—

	Potassium carbonate %	Potassium sulphate %	Potassium chloride %	Sodium carbonate %	Insoluble %
1st grade	93.0	0.5	2.0	4.5	0.04
2nd grade	87.0	5.1	4.9	2.7	0.07

### Vegetable Sources

(a) *Molasses* —Investigations on the recovery of potassium salts from molasses (5–15%  $K_2O$ ) are being conducted by Dr A V Varadaraja Iyengar at the Indian Institute of Science, Bangalore, Professor P Ray and Dr B K Mukherji at the University College of Science, Calcutta, and Mr Walawaker, financed by the Department of the Scientific and Industrial Research. Most of these methods contemplate the use of a reagent which may form an insoluble salt with a potassium compound, capable of regeneration without appreciable loss when the insoluble salt is treated with an acid.

(b) *Bagasse* —The ash of bagasse which is used as a fuel in many sugar factories is obtained as a glassy fused mass containing about 7.5% of potassium oxide.

(c) *Water Hyacinth* —The ash of water hyacinth (about 25%  $K_2O$ ) is a potential source of potassium chloride, but the enormous bulk of the material and the difficulties of collection, desiccation and combustion of the dried material make the prospects of success in this process doubtful.

(d) *Wood, etc* —Dr E J Russell writes of the commercial possibility of the production of potash salts from such forest products as wood, wood waste, hedge clippings and trimmings and saw-mill waste (*Indian Trade Journ*, Vol 39, 1915).

Wood is largely used in India as fuel and the prospects of extraction of soluble potash salts from Indian village ashes have been considered by Mr J W Leather (*Indian Trade Journ*, Vol 38, 1915).

The percentage of potash present in Indian village ashes from various localities as recorded by him are given below —

TABLE I  
*Potash Content of Indian Village Ashes*

	Total	Soluble in Water
Peshawar	1.35	0.21
Lyallpur	2.60	1.15
N.W. Frontier Province	3.26	3.05
Punjab	2.05	1.37
U P, Oris	4.16	1.4
Bombay, Manjri	2.49	
Central Provinces	1.65–4.30	0.16–2.53
Madras, Beswada	1.9	0.53
Bengal	6.7–3.44	3.32–4.28
Assam, Kamrup	10.67	6.88

Leather estimated that the cost of extraction would be about Rs 200 per ton of potash salts and concluded that Indian village ashes can hardly hope to form a useful source of potash. However, these records are very old and it might be worth while to investigate anew the problem of the recovery of potash from this source and from cement kiln dust.

*The Demand for Potash Salts in India*

The bulk of the potash salts required for various purposes is imported from foreign countries Table II shows the import figures for the years 1937-38 to 1941-42 —

TABLE II  
*Imports of Potassic Compounds into British India*

	Quantities in tons				
	1937-38	1938-39	1939-40	1940-41	1941-42
I <i>Manures—</i>					
(a) Muriate of potash	2,928	1,920	2,110	1,585	100
(b) Other potassic manures	1,604	965	1,045	140	
II <i>Chemicals—</i>					
Potassium compounds	2,822	2,118	2,751	2,317	1,707

These imports are principally for Bengal and Madras Presidencies, probably for manuring tea, coffee, cocoanut and rubber plantations

Nowadays, very large quantities of potassium salts are required for the manufacture of such compounds as the dichromate, chlorate, hydroxide, etc. It is computed that 2,000 tons of potassium salts will be required annually in the manufacture of dichromate alone in Bombay, Madras and Mysore

Potassium chlorate is urgently demanded by the Indian match industries in large amounts. Investigations for its manufacture undertaken at the Indian Institute of Science, Bangalore have yielded successful results on a small scale. The Board of Scientific and Industrial Research has recently sanctioned a grant for the erection of a pilot plant for the manufacture of potassium chlorate. The production of the required amount of this salt would also need potassium chloride to the extent of several hundred tons per annum.

*Production of Potash Salts in India*

The sources of potassium salts manufactured in India at the present time are sea-water, certain subterranean brines and the saltpetre industry. No potassium salts are made from Indian lake brines but a few comments on this subject are included to show that this theoretical source of potassium salts has not been overlooked.

*Indian Lake Brines*—In a note on the Lonar Soda Deposit by W. A. K. Christie (*Rec. Geol. Surv. India*, 1912, XLI, 276), analyses are given showing the potash content of various products as ranging from 4.28 to 10.29% potassium oxide, though no mention is made of such notable potassium content in the note on Lonar Lake by E. R. Gee (*Rec. Geol. Surv. Ind.*, 1935, LXX,

438), while, on page 284 of his article (*loc cit*), Dr Christie makes some pertinent comments on the low content of the potassium in the lake water. No attempt has been made to recover potassium salts from this source. Attention is also invited to the note by Dr P K Ghose (*Rec Geol Surv Ind*, 1934, LXVIII, 244) in which he gives analyses of reshta salt (wind salt) from Sambhar Lake (Rajputana Salt Sources) showing 7.3–8.19% potassium oxide. This is somewhat curious, as recent analyses of reshta salt from that source have shown potassium to be absent and that the concentrated East Lake bitterns only contain 0.3–0.4% potassium chloride. One of the most noticeable features of all the brines from Sambhar, Gudha, Nawa, Didwana and Pachbadia is the negligible percentage of potassium salts present.

(1) *Sea*—Exhaustive investigations on the recovery of potassium chloride on a large scale from sea bitterns have been conducted by Messrs Tata Chemicals Ltd, at Mithapur in the Rann of Cutch under the direction of Mr Kapil Ram Vakil, the Technical Director, and the scheme for their manufacture has been completed. Production of potassium chloride has already commenced and the probable output will be 300–400 tons of 85–90% grade salt per annum. The Grax Salt Works recently floated at Karachi also propose to make potassium chloride.

In the salt factories of the Madras Presidency, the bitterns of the density between 29° and 33° Bé containing 5.0% potassium chloride on the solid residue are usually run to waste. Attempts could also be made to obtain the quantity of potassium chloride available from this source and from Madras swamp brines. The method for its recovery has been already worked out in the laboratory of the Indian Institute of Science, Bangalore.

Table III gives an idea of the amount of potassium chloride per litre of bitterns recently determined in the bitterns from a number of places named in Madras Presidency showing a high percentage of the salt.—

TABLE III.

Salt Factory	Grams of potassium chloride per litre of bitterns	Salt Factory.	Grams of potassium chloride per litre of bitterns
Ganjam	21.7	Krishnapatnam	16.9
Covelong	11.8	Chinnaganjam	20.6
Cuddalore	22.8	Balachervu	23.0
Mulapeta	17.2	Sevandakolam	14.4
Markanam	19.8		

Two samples of salt contained—

Sodium chloride 91.0%, potassium chloride 3.7%.

Sodium chloride 89.7%, potassium chloride 7.2%

(2) *Subsoil Brine*—Attempts have been made since 1934 by the Pioneer Magnesia Works Ltd to manufacture potassium chloride from the bitterns obtained after the separation of salt from Kharaghoda brine

The problem of the recovery of potassium chloride was investigated by the late Mr G V Sulabhavi, working in the Royal Institute of Science for the Department of Industries, Bombay. He studied the conditions of separation of carnallite from these bitterns and worked out a process for separation similar to that used in making potassium chloride from Dead Sea brine (*vide* 'A Store House of Chemicals' by M A Novomeysky, 1936, Institute of Chemical Engineers, London), two grades of salt being obtained, 60–65% potassium chloride and 80–85% potassium chloride. About 15 tons of 80% potassium chloride were prepared by Mr Sulabhavi during the course of his experiments. The Pioneer Magnesia Works Ltd have already commenced the manufacture of this important chemical and it is anticipated that about 400 tons of potassium chloride of this quality will be available annually from this source.

(3) *Saltpetre Manufacture and By-products*—An important source of potassium salts in India is the natural occurrence of potassium nitrate in surface soils and efflorescences in many parts of the country.

The manufacture of saltpetre from this source is a very old Indian industry and, before 1860, India was the only country which supplied saltpetre to the world markets.

Large quantities of the salt are found in the United Provinces, Bihar and the Punjab and smaller quantities in Kashmir, the Central Provinces, Bombay and Madras Presidencies and in Burma. It occurs in the surface soil and can be scraped off from November to the commencement of monsoon. The average saltpetre content of these deposits is 3–5%. A full account of them is given by D Hooper (*Agric Ledger*, 1905, 12, 23), J W Leather, J N Mukherjee (*Agric Res Inst Pusa Bull*, 1911, 24), C M Hutchinson (*ibid*, 1917, 68) and in 'The Salt Industry in India' by S C Aggarwal, 1937, Government of India Press.

Details of potassium nitrate manufacture will not be given in this paper but attention is drawn to the considerable quantities of potassium chloride and, to a less degree, of potassium sulphate which may be obtained as a by-product of this industry.

When the crude saltpetre is received at the refineries from the districts, it is treated with water in a pan and the liquor is brought to the boil. The liquor is run off and leaves a residue which is called 'sitta' and is taxable at Re 0.1-3 per maund. The analyses given below show that this substance has a very variable composition depending on the competence of the refinery making it, but in all cases it contains a high percentage of potassium chloride and sodium chloride —

TABLE IV

*Sitta*

	%	%	%	%
Insoluble	4 75	16 34	2 20	2 16
Calcium sulphate	1 62	2 21	1 10	0 75
Potassium sulphate	12 15			2 15
Potassium nitrate	12 13	8 08		5 05
Potassium chloride	37 30	23 57	18 0	37 23
Sodium chloride	32 07	43 96	58 51	43 83
Moisture		3 90	2 83	6 66
Magnesium sulphate		1 39		1 88
Sodium sulphate		0 44	17 10	
Sodium carbonate		0 07		0 15
Sodium bicarbonate		0 14		0 23

When potassium chloride is separated from *sitta*, sodium chloride also crystallises out and is called 'refinery salt' and is taxable at the rate of ten annas per maund 'Papri' (analysis below) is a by-product of this separation

TABLE V

*Papri*

	%
Moisture	0 51
Insoluble	0 86
Calcium sulphate	0 61
Potassium nitrate	4 04
Potassium chloride	18 51
Sodium chloride	49 72
Sodium sulphate	25 63
Sodium carbonate	0 15
Sodium bicarbonate	0 04

The qualities of potassium chloride obtained in this way are indicated by the analyses in Table VI. It is used largely as a manure

TABLE VI

*Potassium Chloride*

	%	%	%	%	%
Moisture	1 75	1 14	2 50	5 30	2 18
Insoluble	9 50	1 86	3 40	0 20	0 24
Sodium carbonate	0 38	0 28			
Sodium bicarbonate	0 48	0 19			
Calcium sulphate	5 52	0 94	2 38		
Magnesium sulphate	1 53	2 09			
Potassium sulphate	19 15	10 74			
Potassium nitrate	0 67	0 48			
Potassium chloride	49 08	62 13	58 26	86 16	95 54
Sodium chloride	11 19	20 82	32 75	2 42	3 28
Sodium sulphate			0 43	5 84	0 46

The all-India figures are not readily available, but the authors are indebted to the Collector, Central Excises and Salt, North-Western India, for the following information relating to the West Central Division in which there were sixty-six saltpetre refineries operating in the year 1940-41. They produced 272,416 maunds of refined saltpetre containing 90% potassium nitrate, or better, and about 300,000 maunds of sitta, papri and potassium chloride. Excluding the third analysis of sitta, an inferior specimen, it is fair to say that the content of potassium chloride does not average less than 33%. Hence, in the West Central Division of North-Western India alone, potassium chloride in sitta is available to the extent of one lakh maunds or nearly 3,500 tons. Considering the extent of the saltpetre industry in India, the figures for the whole country must be very much greater.

Even if the three sources mentioned above were fully exploited, the amount of the potassium chloride produced would probably not meet the total demand of the country. It is expedient, therefore, that attempts should be made to investigate the possibility of manufacturing potassium chloride from other Indian sources on an economic basis and it is hoped that those engaged on this important work will shortly be able to give India the benefit of their enquiries.

# TECHNICAL PRODUCTION OF POTASSIUM PERMANGANATE AND THE EXTRACTION OF POTASH SALTS IN INDIA

By PRIYADARANJAN RAY, *University College of Science, Calcutta*

(*Read at Symposium, April 19, 1941*)

In this paper I would like to discuss briefly the possibility of preparing, on a large scale, potassium permanganate, potassium carbonate and other potassium salts in India, in which I have been interested for some time. To begin with, I should mention that the manufacture of potassium permanganate has already been undertaken by the Bengal Chemical & Pharmaceutical Works, Ltd., in Calcutta and their product is, I believe, already on the market.

Regarding the manufacture of potassium permanganate it is nowadays possible, according to the latest method, to oxidise as much as 99% of  $\text{MnO}_2$  of the pyrolusite to potassium manganate, which is then converted by electrolytic oxidation to permanganate. All the necessary conditions for the successful working of the process have been thoroughly worked out by the above-mentioned firm and it can reasonably be expected that the manufacture of this chemical is not likely to be affected by foreign competition after the war, provided, of course, the supply of potash at a moderate cost is always maintained. Before the war practically the whole of our supply of potash used to come from Germany. Since then, however, India has had to depend for its potash supply on Japan and America. If this supply is cut off, as it might be in the near future, this nascent industry will be seriously threatened. As for the other raw material, pyrolusite, India is fortunately independent of foreign supply. It is, therefore, high time to tap all possible sources of potassium compounds in India and try to develop methods for their extraction.

A fruitful source of potash salts is, as is well known, found in this country in the naturally occurring nitre beds. Potassium carbonate is now being prepared by several firms from this natural nitre and even exported in quantities to such a distant country like Australia. The method adopted for the conversion of nitre into potassium carbonate cannot, however, be considered economical, as it destroys the valuable nitrogen. Besides, even if the whole of the potash thus produced be consumed within the country, it can at most meet only a very small portion of our pressing demand. This makes it imperative to search for other available sources of potash in the country. I shall now discuss here some possible sources, which, in my opinion, offer promise of economic exploitation not only during the present war conditions, but also even after the end of the war against foreign competition. I shall deal with these sources, one by one, according to their relative importance.

### 1 Potash from Molasses

Molasses from Indian cane-sugar industry have been found to be very rich in potassium salts. An average composition of molasses from Indian factories, as analysed in our laboratory, is given by —

Ash = 11.3–12.3,  $\text{SiO}_2$  = 0.18,  $\text{P}_2\text{O}_5$  = 0.10,  $\text{SO}_3$  = 1.30,  $\text{Cl}$  = 0.70,  
 $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  = 0.043,  $\text{CaO}$  = 1.22,  $\text{MgO}$  = 0.28,  $\text{K}_2\text{O}$  = 5.15,  
 $\text{Na}_2\text{O}$  = 0.24,  $\text{CO}_2$  (by diff.) = 2.3%

This shows that about 50% of the ash consist of potassium compounds, or from every ton of molasses at least one cwt. of potassium salts can be recovered. If the Indian factories remove most of the crystallisable sugar from molasses, or if this sugar is previously removed by fermentation into alcohol, the residue will be still more rich in potash salts.

We are at present investigating the economic possibility of extracting the potash from molasses, which is likely to yield different kinds of potassium salts such as carbonate, chloride and sulphate. The work is being subsidised by the Board of Scientific and Industrial Research.

A method of extracting potassium salts directly from molasses has also been suggested by a French worker, Caspar Y Arnal (*Chem Ind*, 20, 1928, 27, T 27). The process is worth a trial. It consists in precipitating the potassium salts from molasses by calcium ferrocyanide in the form of calcium potassium ferrocyanide,  $\text{CaK}_2[\text{Fe}(\text{CN})_6]$ , which is then decomposed by ferric sulphate when a solution of potassium sulphate containing some calcium sulphate is obtained, and the residue of Prussian blue is then treated with lime for the recovery of calcium ferrocyanide.

Methods have been suggested for the separation of potash from molasses in the form of potassium acid tartrate or potash alum. Neither of them can lead to a complete separation of the potash salts from molasses nor to a complete recovery of the reagent employed. These are, therefore, of little technical significance.

### 2 Potash from Wool Scourings

Another rich source of potash salts is furnished from washings of sheep's wool. The crude unwashed wool contains about 10% of potassium salts of stearic, oleic and other organic fatty acids as well as a little chloride and sulphate. If these washings are collected, for instance, at Kashmir or even at the factories at Cawnpore and then evaporated the residue can be easily treated for the preparation of potash salts. Sheep's grease can also be obtained as a by-product. Notable quantities of potash salts are obtained from this source in France, Belgium, Germany and America.

### 3. Potash from Plant Ashes

It is well known that ashes from land plants are rich in potassium salts and constituted one of the earliest sources of potash. Of these, special mention may be made of the following —

Ash of plants	K <sub>2</sub> O-content
Sun-flower stem	36-37%
Chrysanthemum tegetum	24-25%
Cotton husk	10-42%
Banana stem	46-64%
Banana skin	57-58%
Bamboo shoots	32-33%

Extraction of potash from the last four sources is well worth a trial

#### 4 *Potassium Salts from Sea-water*

The mother liquor from the separation of common salt also furnishes quite a rich source of potassium and magnesium salts. The average K<sub>2</sub>O-content of sea-water is 0.04%. About 18-40 gms of KCl per litre have been found in the mother liquor remaining after the separation of common salt from sea-water. Potassium salts can be recovered from this without much difficulty either by stepwise or fractional crystallisation, or in a single step in a very pure form with the help of dipicrylamine.

#### 5 *Potassium Salts from Felspar*

Several methods have already been patented in Germany and the United States of America for the preparation of potassium salts from felspar, mica dust and other potassium-containing silicate rocks, which may contain 10-15% of K<sub>2</sub>O. In some of these patents claims have been made for a recovery of as much as 80-90% of potassium present in the silicate rocks. Neither time nor space will allow me to go into details of these processes, though many of them appear quite attractive and promising with a prospect of giving rise to important by-products like cement and fertiliser.

An intensive work along all these separate lines is likely to lead sooner or later to some important developments in the potash industry in this land.

Finally, it will not be out of place to quote here the annual imports of potassium compounds in our country and their total values. These include bichromate, chlorate, cyanide, permanganate and other compounds:

Year	Quantity	Value in rupees
1934-35	47,537 cwt	13,05,428
1935-36	65,332 ..	16,32,964
1936-37 ..	49,072 ..	11,38,980
1937-38 ..	56,434 ..	12,00,780
1938-39 ..	42,360 ..	11,08,545



## PHOSPHATE FERTILISERS

By N JAYARAMAN, *The Indian Institute of Science, Bangalore*

(*Read at Symposium, April 19, 1941*)

The use of phosphatic materials as fertilisers was practised from a very early period. As the practice is very old it is not possible to find out when and where it originated. These materials, especially bone, fish and guano, were largely used without understanding the real significance in using such materials. The increase in crop yield resulting from the use of such materials was attributed to various causes. It was only after the discovery of phosphorus and phosphoric acid that it was recognised that this effect was due to the phosphorus present in those materials. From this stage onwards the use of phosphatic materials as fertilisers progressed rapidly and new methods were discovered to apply phosphorus to the soil in a form in which it would be readily available for the plants.

Before proceeding further, it is necessary to give an idea of the function of phosphoric acid in plant nutrition. Even though the amount of phosphorus finally retained by the plant is very small compared to the amount supplied, it greatly helps the plant in various other ways. While nitrogen promotes growth and delays maturity, phosphorus promotes maturity. It is closely related to the grain formation of the crop and almost always found in large proportions in the reproductive parts of the plant. It is generally considered to promote the rapid ripening of the grain. Further, its presence tends to increase the proportion of grain to straw. It stimulates the early development of the young seedling to a very great extent. The presence of large quantities of this element also keeps the soil in a very good mechanical condition and thereby indirectly helps the root system of the plant to develop vigorously.

The sources of phosphates are (i) bones, (ii) mineral phosphate, and (iii) basic slag. Even though bone and guano were used for the manufacture of superphosphate in earlier days, now superphosphate and other phosphate materials are mostly prepared from mineral phosphates. At present bone is used either in the raw state as bone meal or as a manufactured product as steamed or degreased material. So, here it is proposed to deal mainly with the mineral phosphates.

Phosphorus is one of the constituents of the lithosphere (earth's crust) and there it occurs mainly as calcium phosphate. This calcium phosphate can be classified under two main heads according to the nature of its origin. They are (i) primary, and (ii) secondary. The primary material occurs as the well crystallised (hexagonal) mineral, apatite. This mineral is of igneous

origin. Two varieties of apatite have been recognised and they are (i) fluor-apatite  $\text{Ca}_5(\text{PO}_4)_3\text{CaF}_2$ , and (ii) chlor-apatite  $\text{Ca}_5(\text{PO}_4)_3\text{CaCl}_2$ .

The secondary material occurs as an amorphous product. As it occurs in large deposits it is generally recognised as 'rock phosphate'. The deposits of this rock phosphate can be classified roughly under three heads according to their mode of origin. They are (i) residual, (ii) replacement, and (iii) sedimentary deposits. The residual deposit is the one which is derived from a deposit of phosphatic limestone due to weathering and other denuding agencies. Replacement deposits are brought about by the gradual conversion of limestone deposits by the action of phosphate-bearing solutions. Most of the Ocean Island deposits belong to this category. They can be considered as mineralised guano deposits because the phosphorus is principally derived from guano.

Sedimentary deposits are those which result from the gradual accumulation of phosphatic material in sea bottom. These later on get raised above sea level and occur interbedded with other sedimentary rocks. This rock is also considered to be of organic origin. This type of sedimentary deposits contributes the main bulk of the rock phosphate of commerce. Workable deposits of phosphate rock have been found to occur throughout the world. Some of the world-famous deposits occur in America and North Africa (Algeria, Morocco and Tunisia) and in some of the Ocean Islands. The following table gives the approximate yearly world production and reserve of phosphate rock. (An approximate average for the period 1930-35 is given in tons.)

TABLE I

Countries	Production	Reserve *	Grade-average % of $\text{Ca}_3(\text{PO}_4)_2$
United States	4,000,000	7,000,000,000	65
North Africa { Tunisia Algeria Morocco Egypt	3,500,000	1,000,000,000	63
	1,000,000	1,500,000,000	63
	2,000,000	1,500,000,000	75
	350,000	200,000,000	60
Nauru and Ocean Islands	700,000	200,000,000	83
Russia (both European and Asiatic)		6,000,000,000	below 50
India { Apatite Sedimentary rock phosphate	300	500,000	85
	nil	8,500,000	57
TOTAL	11,550,300	17,400,000,000	

Many methods have been suggested, patented and used to prepare soluble phosphates from these naturally occurring insoluble phosphates. These can

\* Estimated from known deposits.

be classified as follows: (1) Acid treatment, (2) volatilisation, (3) decomposition by some cheap reagents at high temperature, and (4) as a by-product of steel industry (basic slag). Of these the first one is the most important and universally employed. The acid employed for this process is sulphuric acid. Nearly 50% of the world's production of this acid is utilised for this purpose. In the resulting product of acid treatment, known as superphosphate, most of the phosphorus is present in a water-soluble state as monocalcium phosphate. If excess of sulphuric acid is added, free phosphoric acid is formed. For the preparation of a concentrated superphosphate (double super) phosphoric acid obtained by treating rock phosphate with excess of sulphuric acid is utilised to treat fresh charges of phosphate rock. Most of the superphosphate and other phosphate fertilisers consumed in India are of foreign origin and are prepared from rock phosphate. The small amount that is produced in India is from bone ash and bone char which are the by-products of other industries.

Next in importance is the volatilisation process by which the natural phosphate is heated strongly with some reducing agents and silica and the volatilised elemental phosphorus is again converted into phosphoric acid. Only a small portion of the acid prepared by this process is at present utilised for the production of concentrated fertilisers. Even though this process has not yet advanced very much, it can be safely predicted that it has very good future.

In addition to these methods a number of processes have been invented for decomposing the tricalcium phosphate in the natural phosphates by calcining them with various cheap reagents, such as silica, etc. The resulting materials are similar to basic slag in their crop-producing powers. A German product of this process, called Rhenania phosphate, is extensively produced and sold. The available phosphate in this material is not present in a water-soluble state, but, as in basic slag, they are soluble in a 2% solution of citric acid. The great advantage with this process is that it eliminates the use of sulphuric acid and helps us to utilise even very inferior grades of rock phosphate. Thus the cost of the resulting material is reduced considerably.

Basic slag is obtained as a by-product from the steel industry. The phosphorus present in this material is mainly derived from the iron ore used for producing pig iron and as such it could be considered as of mineral origin.

A general survey of foreign literature on the mineral phosphate deposits of the world reveals the complete absence of any reference to the occurrence of the phosphate deposits in India. As the primary industry of India is agriculture the very limited occurrence of phosphatic rock in India should be very much regretted. At present even this limited stock is not being utilised.

The only occurrence of phosphatic deposit on a sufficient scale is near Trichinopoly. Here the phosphorus present as tricalcium phosphate occurs in the form of nodules along with calcium carbonate and calcium fluoride. These nodules occur in the cretaceous beds of the Perambalur Taluq, Trichy.

District. The quantity available is about 8,000,000 tons. A similar deposit overlying the Deoban limestone occurs near Mussoorie. Apatite in massive and crystalline form occurs at various localities in India.

While India exports annually more than 80,000 tons of bone valued at Rs 90 lakhs, she imports finished phosphate fertilisers of the value of 15 lakhs.

As the Trichy rock phosphate deposit is situated very close to the agricultural tracts of Tanjore and Trichy Districts, it is highly essential that ways and means should be found for supplying phosphorus to these tracts from this deposit.

For the present scheme of work extensive investigations were carried out to find out whether it is possible to eliminate the impurities which stand in the way of using this material for the production of superphosphate. After grinding the phosphatic rock, which occur as flint-like nodules, into fine powder (100 or 80 mesh) it was subjected to various mechanical treatments. It was first treated with an air-separator. The heavy concentrate showed an increase in its phosphorus content while in the tailings an enormous reduction in the phosphorus content and a substantial increase in the calcium carbonate content was noticed. After this, concentration by Wilfley Table was resorted to find out the conditions under which the maximum yield with a minimum loss could be obtained. Experiments with samples of different particle sizes (60, 80 and 100 mesh) were tried and it was found that the sample having a particle size between 80 and 100 mesh was the best suited for the purpose. No doubt, concentration by Wilfley Table results in some loss of material and thus can be prevented only with great difficulty. By heating the material before putting it on the Wilfley Table the process also works out well. By this procedure the loss of material is considerably reduced. Further, as the organic matter is also destroyed the resulting material shows a further increase in the phosphorus content. But, one serious objection would be the large amount of fuel consumed which naturally raises the cost of concentration. This method can be adopted if the fuel is obtained cheap.

(The results of these experiments are given in Table III.) The slight increase in the phosphorus content shown by the ignited specimen is probably brought about by the loss of organic matter, combined water and  $\text{CO}_2$ . But even though the material resulting from ignition shows a slightly enhanced phosphorus content, still it could not be used for the production of acid phosphate. Because, the calcium, which was originally present as calcium carbonate, was still present as lime and so it would readily combine with sulphuric acid to form gypsum.

In Table II a complete analysis of an average sample of phosphatic nodule powder along with the calculated mineral composition is given.

TABLE II

Oxides and other constituents	Composition of the phosphatic nodules per cent	
	Chemical composition	Mineral composition
Moisture	1.37	
Combined water and organic matter	5.02	
SiO <sub>2</sub>	3.08	
P <sub>2</sub> O <sub>5</sub>	27.08	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> 59.13
CaO	43.30	Gypsum 3.25 CaSO <sub>4</sub> ·2H <sub>2</sub> O
Fe <sub>2</sub> O <sub>3</sub>	2.53	
Al <sub>2</sub> O <sub>3</sub>	2.83	
MgO	0.96	
SrO	1.75	Celestite SrSO <sub>4</sub> 3.10
K <sub>2</sub> O } Na <sub>2</sub> O }	Trace	
SO <sub>3</sub>	3.26	
CO <sub>2</sub>	5.63	CaCO <sub>3</sub> 12.80
F ..	2.65	CaF <sub>2</sub> 7.45
Arsonic was absent		
TOTAL	99.46	

TABLE III

*Results of concentration of the nodule powder*

Constituents	Nodule		Calculated at * 950°C for 7 hours	Concentrate † 62 lb from 100 lb
	1a	1b	2	3
Moisture (110°C)	1.37	1.37		0.72
Combined H <sub>2</sub> O and organic matter	5.02	5.02		0.61
SiO <sub>2</sub>	3.08	4.98	6.30	4.70
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	59.13	61.30	67.10	80.10
CaCO <sub>3</sub>	12.80	10.60		1.00
CaF <sub>2</sub>	7.45	5.30		6.20
Fe <sub>2</sub> O <sub>3</sub>	2.53	2.60		1.00
Al <sub>2</sub> O <sub>3</sub>	2.83	4.70		2.30
MgO	0.96	0.42		0.14
SrSO <sub>4</sub>	3.10	2.15		
celestite. CaSO <sub>4</sub> ·2H <sub>2</sub> O	3.25	2.02		1.30

NB—The celestite which is recovered as a heavy concentrate can be considered as a valuable by-product

\* Calcination was done with 10 lb samples for 7 hours at 950°C Yield = 8.7 lb

† Wilfley Table separation was carried out with 100 lb of calcined material Table tilt = 5° and number of vibrations of the table per minute = 120 Yield of concentrate = 62 lb

*The calculated cost of the concentrated nodule powder*—The cost of the phosphatic nodule has not yet been fixed, but at present it can be had for Rs.12 per ton at Trichy or Rs 10 on the spot

Cost of grinding 1 ton of the phosphatic nodule to 80 mesh or 100 mesh powder	Rs 5
Cost of concentrating 1 ton of the powdered ore by the Wilfley Table before heating the material	. „ 5
Do. do after heating the material	. „ 10

So the cost of one ton of concentrated nodule powder at Trichy would be roughly Rs 50. Thus it would work out to be much cheaper than bone ash which contains almost the same amount of  $\text{Ca}_3(\text{PO}_4)_2$ . It would be economic to use this material for the preparation of acid phosphate only when a cheap supply of sulphuric acid is available.

Owing to the very high cost of sulphuric acid prevailing at present it does not appear to be a profitable proposition to prepare superphosphate from the phosphatic nodule powder even after it is well concentrated. It will be successful only if the cost of sulphuric acid is reduced considerably, and this is not possible under the present circumstances in which sulphuric acid is being manufactured in India. So experiments were conducted to study the various other processes by which a quick-acting phosphatic fertiliser could be produced without using sulphuric acid.

With the object of eliminating the use of sulphuric acid for the preparation of quick-acting phosphate fertilisers from rock phosphates, numerous investigators have worked on the calcination processes in which the natural phosphate is heated in a powdered condition with cheap reagents which could be obtained anywhere. The resulting material contains either the whole or part of the phosphorus present in the rock in a form which is readily available for plants. Almost all the processes discovered so far are covered by patents and most of them are not being worked at present owing to the low cost of superphosphate available in those countries in which the patent rights are being held. Further, it appears that these processes would work satisfactorily only so far as a definite type of phosphate rock is treated. Because, the proportions of cheap reagents which are to be added to the phosphate rock depends entirely on the particular grade and composition of the phosphate rock.

For the present scheme of work some of the old processes were tried but they failed to give satisfactory results. So experiments were carried out using varying proportions of some of the cheap reagents which are readily available in South India and a process has been worked out which has given satisfactory preliminary results.

For this process the phosphatic rock and the other ingredients should be finely powdered and the powdered material should completely pass through a 100 mesh sieve.

*The Process*—Certain proportions of the phosphatic rock powder, silica (sand or quartz) or potash feldspar, gypsum and an iron-manganese ore were thoroughly mixed and this mixture was heated in a slow current of air (oxidising atmosphere) at a temperature range of 1,100°C to 1,200°C for 45 minutes while it was kept constantly agitated to expose fresh surfaces. The resulting sintered mass was cooled suddenly. It was observed that it has formed very soft clinkers which could be easily crushed into fine powder. This resulting material contained as high as 16% citrate soluble  $P_2O_5$  (determined by Wagner's citric acid method) while before ignition it held only 1.2% citrate soluble  $P_2O_5$ . Heating the phosphate rock with silica or potash feldspar and alumina or magnesia, while it kept the resulting material in an excellent mechanical condition, yielded a definitely lower quantity of citrate soluble  $P_2O_5$ —10 to 11%.

One very great advantage in using potash feldspar instead of silica is that most of the  $K_2O$  in the feldspar is converted into a citrate soluble form in which it is readily available for plants.

TABLE IV  
Chemical composition of the various ingredients used  
Per cent

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	MnO	K <sub>2</sub> O	Na <sub>2</sub> O	CO <sub>2</sub>	CaSO <sub>4</sub>
Phosphate rock	3.5	3.0	2.5	43.30	1	27				5.7	
Silica (quartz)	97	0.7	1.1								
Potash feldspar	66.4	18.9	0.28					12.5	2.7		
Alumina (bauxite)	4.3	68.5	1.45								
Magnesia (magnesite)	2.0		trace	1.23	45.6					46.2	
Gypsum	2.73										91
Iron manganese ore (from Sandur)	3.2		49.7				32.5				

The citrate soluble  $P_2O_5$  and  $K_2O$  were determined by the Wagner's citric acid method. From the 2% citric acid solution holding both the phosphorus and the potash the former was determined by precipitating it both by the molybdate method and by the magnesia mixture method. The potash was determined by the cobaltinitrite method after eliminating the phosphorus by precipitating it with magnesia mixture.

*Large-scale experiments*—Some large-scale experiments using 50 and 30 lb samples were carried out in the Mysore Glass and Enamel Factory (Bangalore) with the kind permission of the Manager of the factory. The various samples were heated in the glass melting pots for a period of half an hour. These experiments proved to be very successful in spite of the fact that the proper conditions of treatment could not be kept up owing to the nature of the pot in which heating was carried out. The heated mass could not be agitated properly and a strictly oxidising atmosphere could not be maintained. The temperature was also slightly lower than what is required for the complete

conversion. While complete conversion results in the material being turned into a soft, friable clinkery mass, the samples heated in the glass melting pots remained powdery. Small portions of this material which were in contact with the hottest part of the pot for a longer period developed clinkers which in one experiment gave as high as 18.3% citrate soluble  $P_2O_5$  and 4% citrate soluble  $K_2O$ . The rest of the mass which was in a powdery state gave only 12% citrate soluble  $P_2O_5$  and 4%  $K_2O$ . The percentage of citrate soluble  $K_2O$  was found to remain constant even under conditions of a large variation in temperature. But at slightly higher temperatures and on continued heating part of the total  $K_2O$  present in the original sample is lost.

Thus these experiments show that if a miniature portland cement kiln is utilised for heating this material under proper conditions a better yield of available  $P_2O_5$  could be obtained. It is highly probable that a product quite as rich in available  $P_2O_5$  as ordinary superphosphate could be obtained. Further, the presence of about 4% of available  $K_2O$ , a very valuable plant food makes this process very attractive. The cost of this material would be also definitely less than the peace-time cost of superphosphate having 18% water soluble  $P_2O_5$ .

Before concluding this article I would like to mention a word about the position of the phosphate fertiliser trade in India. Of course at present it is in a very unsatisfactory state. Many of these phosphate fertilisers are being sold to farmers by reputable firms without informing them as to the amount of available phosphates present in their fertilisers. Many compound and mixed fertilisers under various names are being put in the market without giving any idea as to their composition. The farmer is very much handicapped by such a procedure and he does not know which would be the most suitable for his land and whether he is recovering his money's worth. So it is highly necessary that strict Government control of this trade should be exercised as early as possible to bring about satisfactory market conditions.

## ACETIC ACID

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*(Read at Symposium, April 19, 1941)*

This important compound or its derivatives, organic and inorganic, are extensively used in various industries. By itself it is widely used as solvent, in nitration operations, in the preparation of vinegar and pickles. Enormous quantities are used in coal-tar colour industries. For indigo alone the annual consumption is about 3,000 tons. It is the chief ingredient, besides its important derivative acetic anhydride, in the preparation of cellulose acetate—the basic material for the preparation of acetate silk, toys, cinematographic and photographic films, cellophane paper and lacquer varnish. It is extensively used in the preparation of various esters used in synthetic fruit essences and important synthetic perfumes. Ethyl acetate and amyl acetate, besides being used in flavouring agents, are well known as solvents. Benzyl acetate, terpinyl acetate, geranyl acetate are indispensable in synthetic perfumes. Both acetyl chloride and acetic anhydride, which are derived from acetic acid, are extensively used in organic operations. The well-known drugs aspirin and antifebrin are derived from acetyl chloride and acetic acid.

Many metallic acetates are used as mordants for cloth dyeing, *e.g.*, aluminum acetate, iron acetate, chromium acetate, copper acetate. Basic lead acetate is used in medicine. Cupric acetates besides their uses as mordants give various grades of colour known as verdigris. The well-known pigment white lead is derived from lead acetate.

The foregoing uses would indicate that acetic acid is a basic product for numerous chemical industries. In fact, like its partner sulphuric acid in the inorganic field, acetic acid may be considered to give a definite pointer in consumption to the degree of development of organic chemical industries in a country. India mainly imports finished goods, chemicals and drugs derived from acetic acid; her imports of acetic acid and vinegar in 1937-38 were worth Rs 1,74,000 (7,271 cwt) and Rs 20,331 (18,429 gallons) respectively. Her production in the only wood distillation works of Bhadravati as calcium acetate is about 15-16 tons per year most of which is taken by ordnance factories where acetone is prepared from it.

There are the following sources for the preparation of acetic acid —

- (a) Wood distillation
- (b) Acetic fermentation of molasses
- (c) Oxidation of ethyl alcohol
- (d) Acetylene (from calcium carbide)

Pyroligneous acid, derived from wood distillation, has the following composition —

7-10%	acetic acid
1-2%	methyl alcohol
0.1-0.5%	acetone
Rest	water and other impurities

This is neutralised with lime—methyl alcohol and acetone distilled and the acetate solution is concentrated and then dried whence grey acetate of lime is obtained. There are various methods of obtaining acetic acid, e.g.,

- (1) Grey acetate of lime  $\xrightarrow{\text{Conc } \text{H}_2\text{SO}_4}$  70-75% acetic acid
- (2) Grey acetate of lime + sodium pyrosulphate  $\rightarrow$  90% acetic acid
- (3) Grey acetate of lime (80%) + acetic acid (60%) + 92%  $\text{H}_2\text{SO}_4 \rightarrow$   
glacial acetic acid
- (4) Grey acetate of lime  $\rightarrow$  dil acetic acid (70-75%)  $\rightarrow$  sodium  
acetate  $\xrightarrow{\text{Conc } \text{H}_2\text{SO}_4}$  glacial acetic acid
- (5) Dil acetic acid (70-75%)  $\xrightarrow{\text{azeotropic distillation}}$  glacial acetic acid

Attempts are being made in Bhadravati and Bangalore to prepare glacial acetic acid by various methods but the cost price seems to be too high (5-6 as a lb whereas Japan landed glacial acetic acid in Calcutta at 3 as a lb). The production of acetic acid by acetic fermentation of molasses is being attempted at Cawnpore. From a very dilute acetic acid 4-5% (granting that other impurities are absent) Dr H D Sen claims to have obtained glacial acetic acid by entrainment with ethyl acetate—a commodity not manufactured in India. The experiments are, however, very interesting.

For the last two years in our laboratory we have been busy with the preparation of acetic acid by the oxidation of alcohol and by hydration of acetylene. We have reached 80% yield by the former and 30% by the latter method. For both these operations various new catalysts are being tried with success. Incidentally we have been able to hit upon some catalysts which act simultaneously as oxidation and esterifying agents. Starting from ethyl alcohol and air, a good yield of ethyl acetate is obtained. We hope to develop this process in the near future. These researches are being subsidised by the Bengal Chemical and Pharmaceutical Works, Ltd, Calcutta.

# THE IMPORTANCE OF SODIUM SILICATE SOLUTIONS AND THE POSSIBILITY OF THEIR MANUFACTURE FROM LOCALLY AVAILABLE RAW MATERIALS

By R C RAY and P B GANGULY, *Science College, Patna*

(*Read at Symposium, April 19, 1941*)

Water glass is an important article of commerce. It is generally obtained as a 30 to 40% solution of sodium silicates having a specific gravity of 1.5 to 1.8. Its earliest application was in the soap industry, where it was largely used as fillers. It has also some detergent action of its own. Soluble silicates are extensively used in industry in the manufacture of paper, as adhesives in the manufacture of fibre containers and laminated wall board,<sup>1</sup> in the textile industry, in the manufacture of vitreous enamels<sup>2</sup> and ceramic glazes, in hardening concrete and for numerous other purposes.

Apart from direct applications, the soluble sodium silicate serves as the starting material for preparing a number of insoluble heavy metal silicates, which find applications in several technical processes. The addition of different salts to silicate solutions form precipitates in the wet way.<sup>3</sup> The exact nature of these insoluble silicates is not clear, as there is reason to believe that colloidal silica is simultaneously formed along with the insoluble silicate.<sup>4</sup> However, such precipitated silicates are useful for a number of technical processes. A precipitated lead silicate is used as compounding material for rubber.<sup>5</sup> The well-known sodium alumino-silicates are the most effective base exchange materials and are extensively used for water softening. Lately they are being used for the disposal of sewage.<sup>6</sup>

Sodium silicate solutions have some characteristic physical properties which make them suitable for certain industrial purposes. It appears that the silicate solution preferentially wets a solid surface. Because of this property silicate solution finds use in reclaiming oily cotton waste. In aqueous solution it sets free the oily drops and the cotton waste is rendered fit for further use. It is because of this preferential wetting of solid surfaces that silicate solutions have been used to accelerate the much desired separation between solid paraffin wax and liquid mineral oil.<sup>7</sup> Another characteristic of silicate solutions is that they possess good spreading properties. A comparison of the spreading properties of industrial alkalies by observing their spreading on glass surface has shown that sodium meta-silicate travels the farthest.<sup>8</sup> Because of this behaviour sodium meta-silicate solutions are preferred for washing glass containers used for storing milk. It has been shown that even a very small residue of oily matter in a milk bottle is a fruitful medium for harbouring bacteria.<sup>9</sup> Sodium meta-silicate solutions remove the last

traces of grease and their use is more effective than that of caustic soda solutions of the same sodium oxide concentration

Sodium silicates also act as inhibitors for certain chemical changes. This property is generally associated with the nature and type of film formed from sodium silicate solutions<sup>10</sup>. Thus the addition of a small amount of sodium silicate at once stops the action of warm sodium carbonate solution on a piece of aluminum foil<sup>11</sup> though in the absence of the silicate the metal dissolves completely with the evolution of hydrogen. The phenomenon is specifically characteristic of silicate solutions, and is connected with the formation of a protective film. Connected with this property is the use of silicate solutions in protecting aluminum tubes used for keeping alkaline cosmetics<sup>12</sup>. At low concentrations silica protects from corrosion pipe systems carrying potable and industrial waters. Waste of oxygen during bleaching is prevented in peroxide baths by means of silicate solution<sup>13</sup>. In these respects the silicate solutions act not by virtue of their alkalinity but on account of the action of silica and the nature of the film it forms.

Connected with their power of altering the interfacial tensions is the use of sodium silicate solutions as dispersion or deflocculating agents. A sufficiently stiff dough of clay can be made quite mobile by the addition of a small amount of silicate solution<sup>14</sup>. Advantage is taken of this property in settling out foreign minerals from clay suspensions and in freeing zinc ores from silicious constituents<sup>15</sup>. The ceramic industry depends a great deal on the supply of sodium silicates. Ceramic wares are decorated with glaze in the composition of which the silicate solution serves the double purpose of supplying its share of sodium oxide and silica, and of keeping the other ingredients in position till the sintering temperature is reached<sup>16</sup>. A plentiful supply of sodium silicates will bring its use more extensively in vogue in the making of artificial stones for flooring. By forcing silicate solutions underground loose earth has been consolidated to fit it for foundation<sup>17</sup>. There is no doubt that if the proper conditions be worked out sodium silicate solutions will be a valuable material for grouting structures damaged during earthquakes. Numerous other applications could be cited, but what has been stated in the foregoing paras. shows clearly that if a plentiful supply of sodium silicate be available very important uses could be made of it.

Certain amounts of sodium silicates are manufactured in India. Sodium silicates manufactured by the Imperial Chemical Industries (India), Ltd., samples of which were supplied to us by the factories from London, contain different proportions of sodium and silica varying from the composition of the meta-silicate to that containing four moles of silica per mole of sodium carbonate<sup>18</sup>. The demand for sodium silicates is large in view of their extensive use in soap, paper, textile, and other industries. It was, therefore, considered worth while to investigate the possibilities of manufacturing sodium silicates from materials easily available in Bihar.

Commercial sodium silicates can be prepared mainly by two processes. In the dry process silicious sand is mixed with sodium carbonate and heated to 1000–1100°C for about 4–5 hours. The molten mass is cooled to solidify, powdered and extracted with water under pressure. A reducing agent like carbon helps the process. In the wet process alkaline lye is heated with infusorial earths in an autoclave. Extraction by sodium carbonate was attempted by this process. Infusorial earths were treated with a concentrated sodium carbonate solution in an autoclave under 100 pounds pressure. Only a fraction of the silicate had gone into solution. Sodium carbonate cannot be an effective substitute for caustic alkali in this method. The dry process is thus more suitable for adoption.

As a source of silica sandstone appears to be the best. River sand is not suitable for the purpose. The sand from the bank of the Sone river contains too much iron and other impurities and when fused with sodium carbonate gives an insoluble glass. The Ganges sand near Patna contains too much aluminium and carbonate. Sandstone of a suitable quality and silica content is available in Sahabad District, and in Manbhum.<sup>19</sup>

As the source of sodium carbonate the utilisation of the large supply of alkali earth (Sajji) available in North Bihar is intended. Extensive deposits are available in Bihar and in many districts of the United Provinces. The United Provinces deposits were examined by Watson and Mukerji<sup>20</sup> who have estimated that four million tons of alkali might be made available per year from this source.

The economic recovery of alkali from Sajji is a problem by itself. Some work is in progress in this laboratory on the possibility of working the Sajji so that it might be an alternative source of sodium carbonate in addition to the soda ash. The deposits available in Bihar have been analysed. They contain about 4½% of soluble matter and about 2½% of sodium carbonate. The easiest method of extraction is to collect the sodium carbonate as an efflorescent deposit from the surface of a moistened stack. The question of developing the method into an organised indigenous process is well worth a careful examination.

Some preliminary trials have given quite satisfactory results. The question of a suitable furnace for the purpose is important as the economic production of the material depends primarily on the efficiency of the furnace.

Of the many commercially important substances that are obtained from sodium silicates, silica gel and artificial zeolites or permutites are of special interest. The silica gel has been extensively used in America and England in the last decade and is finding more and more new applications every year. Its use in Indian industries has been rather meagre. In view, however, of its extensive and varied applications, attempts were made to produce a sample of silica gel in this laboratory. A specimen has been obtained which has practically the same adsorptive capacities as the commercial products.

The silica gel of commerce is a hard glassy material, which looks like large grains of clear quartz sand. These grains are full of fine capillary pores and because of their unique structure are extremely capillary active.<sup>21</sup> It has been estimated that one cubic inch of gel has an internal surface of over an acre. Silica gels find use wherever a solid with a large adsorptive power is desired. They are used as dehydrating agents where large quantities of gases have to be purified and dried as, for example, in the production of solid carbon dioxide. In the control of humidity in air-conditioning plants, in refrigeration, in solvent recovery processes, in the refining of petroleum and as a carrier for many catalysts, silica gels find extensive applications. A unique advantage attaching to the use of silica gel is the ease with which the activity of the gel is regenerated.

The gel can be prepared from sodium silicate by neutralisation by an acid. Prepared in the ordinary way, the mass on drying crumbles to a light opaque powder, which has low adsorptive capacity. By proper control of pH<sup>22</sup> of the solutions after admixture and of concentrations a gel of the desired consistency could be obtained. If dried under controlled conditions, it is obtained in the form of granular glass-like transparent particles. A sample of gel prepared in this laboratory was activated by drawing a current of carbon dioxide free dry air through the heated gel and its adsorptive power was studied by determining the quantity of sulphur dioxide adsorbed. The amount of adsorption compared quite favourably with the data given by Patrick and McGavack.

Another purpose for which sodium silicate solutions were used in this laboratory was in the preparation of a sample of permutite. Sodium permutite used to be prepared by fusion of a mixture of sodium carbonate, alumina and silica. It is now manufactured from sodium silicate and sodium aluminate and obtained in the form of coarse granules. Apart from the use of permutites for the softening of drinking and industrial water, they can be used with great advantage to a problem of great interest to Indian sugar industry. Till the manufacture of power alcohol from molasses develops to its full extent, a large quantity of molasses will still remain unworked. The use of molasses for cattle food has often been suggested but the practical adoption of the method has not been possible so far because of the unsuitability of the untreated molasses for the purpose. Molasses contain about 4 to 5% potash. If the potash could be removed the molasses would serve as cattle food without any injurious effects. The potash could be recovered from the molasses by base exchange with sodium by running a solution over a layer of permutite.

It will thus be seen that on the practical side sodium silicate solutions open up a field vast in extent and fertile in possibilities. On the theoretical side also, its unsolved problems are numerous and fascinating. The variety and scope of enquiries in which soluble silicates are concerned depend partly upon the range of properties inherent in the material and partly upon the diversity of industrial processes in which these characteristics have found use.

There seems reason to hope that the manufacture of sodium silicates will yield fruit from which Indian industries may derive some benefit

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# THE MANUFACTURE OF ANTIMONY METAL IN INDIA

By D D KARVÉ, Poona

(Read at Symposium, April 19, 1941)

Antimony metal is one of the most important secondary metals and is used in a large number of valuable alloys. Before the war most of the requirements of this metal were met by foreign countries and the annual consumption was approximately 400-500 tons. Owing to the manufacture of war materials in India, the need for the manufacture of this metal in the country began to be felt. Rich ores of this metal are available in Chitral State on the borders of India, about 200 miles from Peshawar and before the war the ore was exported to foreign countries, mostly to Germany. The selling price in India of antimony metal was about Rs 600 per ton before the war, while it is now nearly Rs 2,000 per ton.

Antimony, as is well known, is used in the preparation of alloys like type-metal, hard lead, bearing alloy and special steels for the manufacture of bullets. It will, therefore, be realised that any country that wants to develop its metal industries, and especially the war industry, must not be dependent on outside sources for its supply of antimony.

The Star Metal Refinery of Bombay decided to take advantage of the conditions produced by the war and start the manufacture of antimony metal from the Chitral ore, which is mainly 'Stibnite', the sulphide of antimony. The factory is situated in the vicinity of Bombay and the cost of transport is necessarily heavy. Even up to the rail-head in Peshawar the transport by mules and other animals is a very troublesome affair, while the cost of rail transport from Peshawar to Bombay is not negligible.

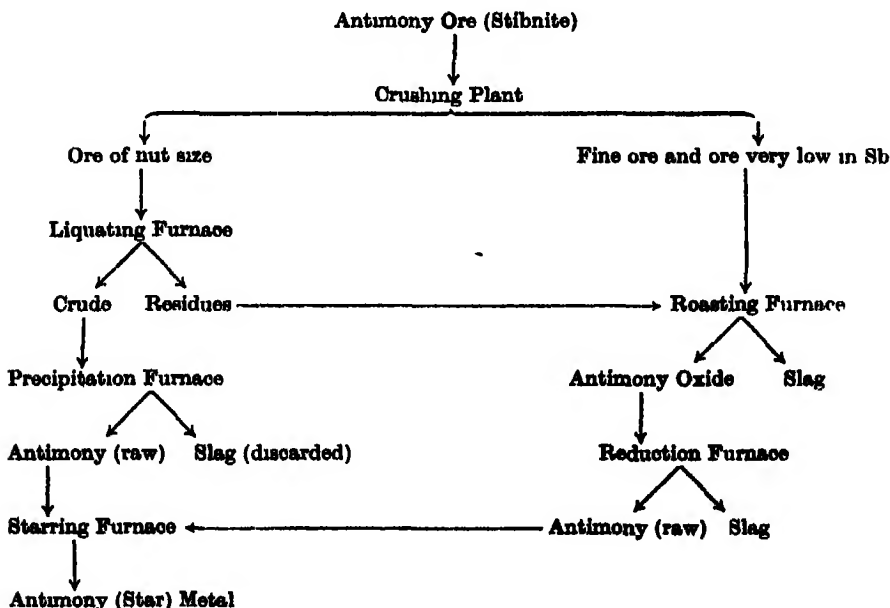
The ore contains from 20 to 65% sulphide. This is crushed and then submitted to the 'liquating' process, which consists of heating the same to about 550°C, when the antimony sulphide begins to fuse and to separate from the gangue or stone. Pure antimony sulphide containing 71.5% of the metal is called 'Crude'. This process is carried out in the 'Liquating Furnace'. The stone or gangue, remaining behind, still contains about 10 to 15% antimony and is called 'Residues'. These are later treated in the 'Roasting Furnace' for final recovery of all the antimony.

In order to recover the metal from the 'Crude', i.e. purified antimony sulphide, it is heated in the 'Precipitating Furnace' with iron scrap and soda ash. The iron combines with the sulphur with the formation of iron sulphide and the antimony is liberated in the form of molten antimony and collects at the bottom of the furnace. It is then tapped and cast into moulds. This impure metal is called 'ingles' and has to be further refined or 'starred' (so called because the crystals of pure antimony have a star-like appearance).

This last operation is carried out in the 'Starring Furnace' Here fluxes are added to remove the last impurities in the form of slag and the ingots obtained show the characteristic star-like crystals on the surface

The recovery of the antimony, still remaining in the 'residues' referred to above, is based on the fact that when antimony metal or 'Crude' is heated to about  $800^{\circ}\text{C}$ , it is oxidised to antimony oxide, which appears like white smoke and can be condensed to a white powder The oxide can then be reduced to the metal by heating it with a suitable reducing agent in the reduction process

The following scheme will make the process easily understandable —



It is expected that the annual Indian consumption of star antimony will go up to 1,000 to 1,500 tons and the factory will be able to meet that demand. It is to be hoped that, once this important chemical industry is firmly established, it will make India independent of outside sources even after the abnormal conditions of the war have disappeared.

I have given the above sketch in the hope that the manufacture of other secondary metals may also be thought of as likely objects of attack by the budding chemical industry of India.

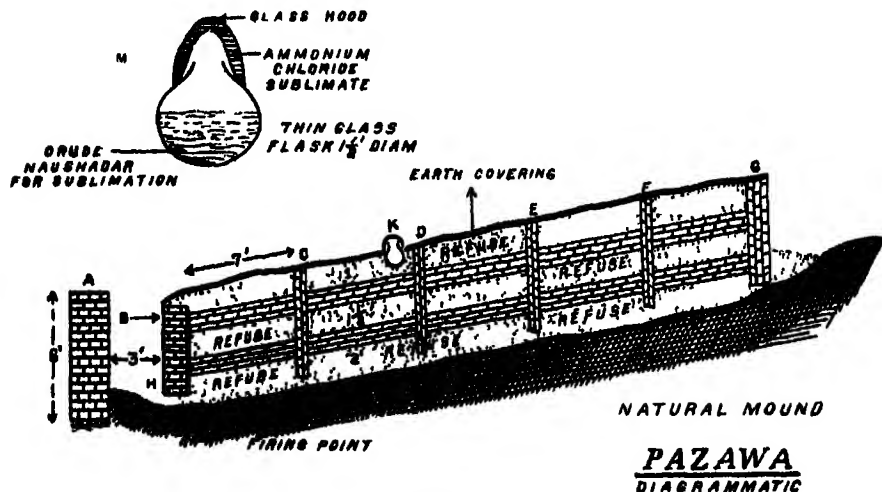
## AMMONIUM CHLORIDE FROM PAZAWAS

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(Read at Symposium, April 19, 1941 )

In Watt's Dictionary of the Economic Products of India, 1889, p 219, it is stated that ammonium chloride or 'naushadar' used to be manufactured by potters (kumhars) in Kangra (Punjab) from village refuse. Apparently, the industry has died out there but, in certain of the tehsils in Patiala State and some villages in Karnal District and Saharanpur, ammonium chloride is still being manufactured in the process of baking crude bricks in village kilns called 'pazawas' which are fired by means of village refuse. This material is collected from time to time and stored until the brick-making season starts towards the end of March.

The process, which differs materially from that described by Watt, is as follows. —



The diagram represents a vertical section through the middle of the length of a pazawa except that, as described below, the vertically placed small bricks shown at C, D, E, F and G are removed before a new section of the pazawa is added.

At the end of the kiln and separated from it is erected a wall, A, about 6' high. At a distance of about 3' from this, a wall, B, is built in which has a hole or bridge, H, through which the kiln is first fired. A layer of dry village refuse 2' thick is laid down and then two or three layers of sun-dried clayey-

mud bricks lying lengthwise and flat are superimposed. Upon this are laid alternately a layer of refuse, a layer of bricks and lastly a third layer of refuse, the whole being usually but not invariably plastered over with mud.

The pazawa is built on a mound at an angle of  $25$  to  $30^\circ$  with the horizontal and is about  $10'$  wide at the base or firing point and gradually widens out until, at the 'free' and upper end, it is about  $40$ – $50'$  wide. Each successively broadening section is about  $7'$  long, the total length of the kiln after two or three months being  $50$ – $60'$ . Thus, the plan of the pazawa is roughly that of a section of a sloping isosceles triangle about  $10'$  at the lower end and  $40$ – $50'$  at the upper extremity.

When the village refuse in the first section is fired, usually with the help of wood fuel in the first instance, it burns slowly and, after some time, ammonium chloride deposits gradually on the layer of smaller damp bricks, *C*, vertically placed at the end of the section at right angles to the general run of the bricks to be baked. Sometimes the bricks are moistened during the process. When the burning has nearly reached the end of the  $7'$  section as shown by the appearance of a white fume, the little bricks, which are now quite dry, are removed and scraped to remove the ammonium chloride containing deposit called 'crude naushadar' which is mixed with more or less earth in the process. This leaves the end 'open', though the fuel in the first section is not entirely consumed.

Another section, about  $7'$  long is then added on to the free end, widening out somewhat and finished off by small vertical damp bricks as before. When white fume again appears, the small bricks are removed as before and scraped, the final pazawa being as shown in the diagram, with the vertical bricks at *C*, *D*, *E*, etc removed.

After the fire in the stack has proceeded to the fourth or fifth stage, the bricks in the earlier sections can be removed progressively after cooling and sold. The total process takes from two to three months.

The number of bricks manufactured in a pazawa varies between  $50,000$  and  $1,50,000$ .

The bricks should be made of 'straight' clay without the addition of sand and the potters say that the smaller the bricks the better the yield of naushadar (crude ammonium chloride) obtained. Sometimes, large pieces of ammonium chloride called 'pāpri' are formed.

Some potters put crude earthy naushadar into earthenware pots (*vide* figure, *K*) which are placed in the upper refuse layer during the slow combustion. By this means, the ammonium chloride is sublimed into a sun-dried clay receptacle. This is ultimately broken to recover the product which is coloured yellow.

If fuel other than village refuse, e.g. wood or coal, is used, ammonium chloride is not formed at all, while it is found that the greater the proportion of cow and camel dung and material of that kind in the refuse, the better the yield of 'naushadar'.

After the burning, much yellowish ash remains which consists mainly of silica and aluminium silicates, with small amounts of iron, sodium and potassium silicates and traces of chlorides. Its potash content is equivalent to about 4.5%  $K_2O$ .

The following gives an idea of the prices obtained for the various products (1941) —

- (1) Crude naushadar is sold for from Rs 2 to Rs 5 per maund depending on the relative amount of earth it contains (13–30%  $NH_4Cl$ ),
- (2) Crude crystals or 'pāpri' (85–92%  $NH_4Cl$ ) are sold at Rs 12 to Rs 15 a maund,
- (3) The yellowish product from K (91–95%  $NH_4Cl$ ) described above which realises about Rs 16 to Rs 20 per maund,
- (4) The 'bells' of whitish salt (over 99%  $NH_4Cl$ ) described in (a) below which fetch Rs 25 to Rs 28 per maund, and
- (5) Pure crystals (99.8%  $NH_4Cl$ ) obtained by process (b) below which are sold at about Rs 35 per maund

The above kinds of crude substance are treated broadly in two different ways —

- (a) By sublimation. The crude material is heated in thin walled vessels made of dark coloured country glass about 18" in diameter and the ammonium chloride is sublimed into 'bells' made of a similar quality thin glass. The whole of the plant is smeared over with several layers of mud. The process is similar to that described in Watt but the flask has no neck. The sublimed ammonium chloride is recovered from the bell by smashing the glass when a thick shell of whitish ammonium chloride is obtained (*vide* Fig 1, M).
- (b) By lixiviation, sedimentation, crystallisation, centrifugalisation and so on. By this more modern process, a very pure product is obtained which sells at Rs 35 a maund, its purity being over 99%  $NH_4Cl$ . A demonstration factory maintained by the Punjab Government is in operation at Kaithal in the Karnal District to instruct villagers in purifying their products.

It has been alleged that the ammonium chloride rises in the clay from the dried ponds and elsewhere by capillary action and that, for this reason, suitable clay is only available at certain times of the year. So far, no specimen of clay received has contained more than traces of ammonium chloride and the proportion of sodium chloride is very small. The village rubbish, as received, contains varying amounts of sodium chloride but no ammonium chloride, the production of this salt being apparently due to a complicated action which takes place during the slow combustion of the village refuse under the peculiar circumstances described.

In the opinion of the writer, this is the source of all of the ammonium chloride produced but the matter needs proper investigation both with the object of discovering if the process could be more widely used as a village industry for the manufacture of ammonium chloride independently of the brick industry, which even now is sometimes subordinate to it, and as an interesting problem dealing with the slow combustion of such material as village refuse of the type used in the pazawas

It was pointed out that this source of  $\text{NH}_4\text{Cl}$  could not compete with that readily obtained as a by-product in the ammonia soda process for making soda ash already established and in course of further development in India, but that, as a village industry, it was worthy of encouragement as serving a worthy purpose where the refuse was not more urgently required as a manure

At the meeting of the National Institute of Sciences held in Delhi on April 19th, 1941, at which the paper was read, a number of members took part in the discussion which followed, notably Sir S S Bhatnagar and Dr J L Sarin, Industrial Chemist, Punjab

In preparing this note, I am indebted to Mr Kashmiri Lal Budhiraja, Chemist to the Patiala Government, for much general information regarding the process and to Mr Manohar Lal, Assistant Chemical Examiner of the Central Revenues Control Laboratory, for collecting and analysing samples from working pazawas

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## MANUFACTURE OF FORMALDEHYDE FROM ETHYL ALCOHOL

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(Read at Symposium, April 19, 1941)

Before the technical production of synthetic resins, the use of formaldehyde was restricted mainly to the preparation of synthetic organic medicinal compounds like hexamethylene-tetramine and of certain synthetic dyestuffs, for example, of the acridine series. But with the advent of phenol-formaldehyde and urea-formaldehyde resins in large quantities in the market, formaldehyde has become one of the important heavy chemicals in modern chemical industries. The starting point for formaldehyde manufacture is as yet methanol, but numerous investigations have been directed towards obtaining the same (formaldehyde) from other raw materials as ethyl alcohol, glycerine, glycol, methane, coalgas, ethylene, carbon monoxide and hydrogen. The use of gaseous catalysts and high frequency electric discharge has also been attempted as means of producing formaldehyde, but as yet these processes are in an experimental stage. The importance of manufacturing formaldehyde from sources other than methyl alcohol would be realised when one takes into consideration the unavailability as yet of cheap methanol in this country. Wood spirit of high and suitable purity is manufactured by the Mysore Iron and Steel Works at Bhadravati, but its price on the spot is of the order of Rs 3-8-0 per gallon. Under best possible conditions, with Rs.3-8-0 per gallon of methyl alcohol, the cost of production of a pound of formalin would be about  $7\frac{1}{2}$  annas at Bhadravati, whereas from synthetic methanol (at 8d to 11d per gallon), the cost would not exceed 2 annas per pound. As a matter of fact, formalin is sold in America at 6 cents = 3 annas per pound, showing thereby that the actual cost of production is somewhat lower than 3 annas per pound. The use of formalin in the manufacture of shellac moulding powders, which has assumed a stage of considerable importance, would require it to be produced at very much lower rates than  $7\frac{1}{2}$  annas a pound, and hence a systematic study of processes for the manufacture of formalin from other sources has been initiated at the laboratories of the Indian Lac Research Institute. The present communication is only one of a series to be published shortly, with ethyl alcohol as the starting material in the first instance, as the latter is readily available throughout India. Under very good working conditions, the cost of production of a gallon of 96% ethyl alcohol would be 5 annas, and the sale price would not exceed 8 annas. This figure of 8 annas per gallon of ethyl alcohol has been taken for the calculation of cost of production of formalin with the result that 1 lb. of formalin costs only  $1\frac{1}{2}$  annas.

The conversion of ethyl alcohol into formaldehyde *via* acetaldehyde, though not unfamiliar, is as yet very little explored. The experimental procedure followed at the Indian Lac Research Institute was as below —

The lay out of the laboratory apparatus —

A 500 c.c. round bottomed flask (A) was provided with a triple bored cork through the holes of which are introduced a thermometer, a tube conveying compressed air and another leading in the vapour of ethyl alcohol and air into the reaction tube (B) containing a roll of copper gauze of 40 mesh and 12 cm. length. The diameter of the roll was 16 mm. which just fitted into the reaction glass tube. The flask (A) containing 200 c.c. rectified spirit was dipped in a water bath so heated that the temperature shown by the thermometer was between 50°–56°C. The compressed air was bubbled at a rate so that five volumes of air corresponded to one volume of ethyl alcohol vapour. This was adjusted by previous calibration. The copper gauze had in its core the thermocouple junction (copper-constantan) the leads of which came out through that end of the reaction tube through which the vapour-air mixture was introduced. The other end of the reaction tube was connected with the absorption system (C, D, E) containing water as shown in the figure. A round bottomed flask and condenser set up between B and C serves as a catch for unconverted alcohol. The exit gases which contained invariably some CO and H<sub>2</sub> together with a large excess of nitrogen were led out into the air.

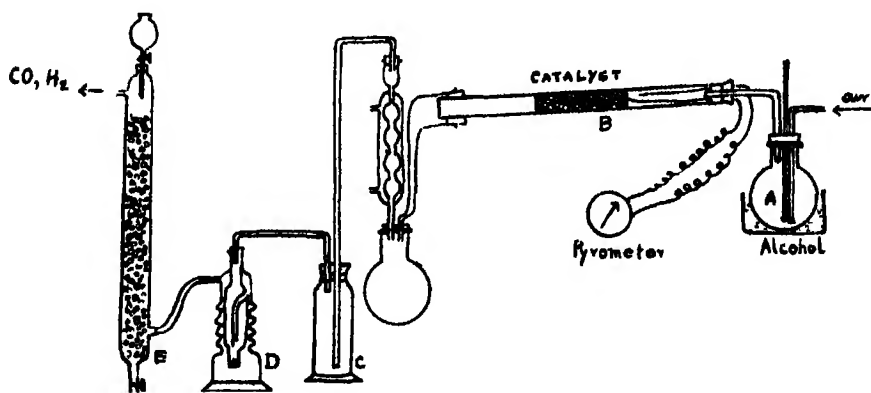


FIG. 1

The copper roll was at first heated to 300°C and the alcohol vapour and air mixture was passed over it. The heating was so regulated by a Bunsen burner or electrically that the temperature did not exceed 350°C. With such a single system, 35 to 40 c.c. of ethyl alcohol could be passed hourly with a conversion into acetaldehyde of as high as 80% of the alcohol passed. By more rapid passage, the percentage of alcohol converted into acetaldehyde decreased considerably, but the total quantity of aldehyde produced per hour could be

substantially increased. For example, 106 c c of ethyl alcohol passed over the copper catalyst in 60 minutes gave 43.4 grams of acetaldehyde, corresponding to 54% conversion, whereas 44 c c of alcohol passed in the same period yielded 26.88 grams of acetaldehyde, corresponding to 80% conversion. The contents of *C*, *D*, and the round bottomed flask are distilled up to 60°C to separate the aldehyde, whilst the water of the scrubber, *E*, is returned to the preceding series. The concentrated aldehyde is then passed through a similar system as described above, but the copper gauze is maintained at a temperature of 450–500°C. A mixture of formaldehyde and acetaldehyde is now obtained which can be separated by fractionation. To illustrate the process, 70 c c of alcohol gave rise to 34 gm of acetaldehyde, which finally on further oxidation gave 6.6 gm of formaldehyde and 14.2 gm of acetaldehyde together with a recovery of 21.2 c c of ethyl alcohol. For the estimation of formaldehyde in the presence of acetaldehyde and ethyl alcohol, the method proposed by Romijn (*Z Anal Ch*, 36, 18, 1897) was followed. In brief, this method consists in estimating total aldehyde by the  $\text{NaHSO}_3$  method and formaldehyde by KCN method. It should be noted here that the method has not been found to be very accurate in our hands. Calculating the yield figures on the basis of the above experiment, 5.75 lb of formalin (40% formaldehyde) are produced per gallon of ethyl alcohol. Taking alcohol at 8 annas per gallon, the raw material cost for 5.75 lb of formalin is only 8 annas. Assuming 20 lb of steam for the fractionation of 5.75 lb of formalin, the cost of the necessary coal is only three pies when coal is taken at Rs 10 per ton. Adding another 6 pies for depreciation, etc the cost of 5.75 lb of formalin works out at 8½ annas or 1.52 annas per lb of formalin, a figure attainable only from very cheap synthetic methanol.

As a comparison, the cost of manufacture of formalin from wood spirit of Mysore Iron and Steel Works, Bhadravati, is detailed below —

	Rs as p
One gallon of C P methyl alcohol	3 8 0
Process charges including depreciation, interest and overhead charges	0 0 9
	<hr/>
Cost of 7.5 lb of formalin	3 8 9
or, 7½ annas per lb	

It would appear that formaldehyde from ethyl alcohol is very much cheaper than that from wood spirit and is practically at the same level of costs as with synthetic methanol.

The separation of formaldehyde from acetaldehyde doubtless brings in complications, but the low cost of ethyl alcohol would appear to justify the introduction of such a process in India, where the disposal of molasses remains as yet an unsolved problem.

The commercial production of formalin in this country would thus appear to be more economical if produced from ethyl alcohol not only now when the only available source of methyl alcohol is from wood distillation, but even at a future date when synthetic methanol might be manufactured in this country. The reason for this is quite obvious when one considers the availability of molasses in very large quantities and at practically no cost in this country. As a matter of fact, the sugar factories with auxiliary plants for the fermentation of molasses could very profitably be manufacturers of formalin, acetaldehyde, ether, acetic acid and ethyl acetate.

# ON THE ELECTROMAGNETIC FIELD AND THE SELF-ENERGY OF MESON

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## ABSTRACT

Assuming Duffin Kemmer's formulation of meson theory the charge distribution, the electromagnetic field and the self-energy of mesons with spins one and zero are discussed. The charge distribution is found to have a high order of singularity and is extended over a finite region of the order of  $\frac{\hbar}{mc}$ . The self energy is calculated by an approximate method which is equivalent to the second order perturbation theory. It is found that the self-energy consists of four different parts which are due to the static field, the transverse electric field, the magnetic field and the forced vibrations under the zero-point fluctuations of the radiation field. The second and the third parts arise from the spin, and so are zero for spinless meson. In terms of the 'cut off momentum'  $P$ , for a meson with spin one these two parts diverge separately as  $P^4$ , but cancel one another to this order resulting a quadratic divergence. The first and the last parts diverge quadratically, and so also the total self-energy for both the particles. The transverse part of the self-energy is also calculated by second order perturbation calculation. The results are compared, in every stage, with the corresponding ones for an electron in the positron theory.

## INTRODUCTION

The self-energy of the electron in Dirac's positron theory was discussed by Weisskopf (1934) by a second order perturbation calculation. This self-energy, as shown by him, diverges logarithmically with infinitely small radius. Later on by an approximate method, which is equivalent to the second order perturbation calculation and is open to the same objection as the perturbation theory, he (Weisskopf, 1939) separated this total result into different parts whose physical causes are more clear than the total one. According to his treatment the different parts of the self-energy of an electron are—(i) the energy due to the longitudinal electric field (Coulomb field), (ii) the energy due to the transverse electric field arising from the oscillatory motion which produces the spin, (iii) the energy due to the magnetic field (also from the spin), and (iv) the energy of the forced vibrations due to the influence of the zero point fluctuations of the radiation field. In terms of the 'cut off momentum'  $P$ , the first part diverges logarithmically, the second, the third and the last parts separately diverge quadratically, but compensate one another to a logarithmic term. In the same paper Weisskopf applied a similar treatment to the Bose particle with spin zero, as has been developed by Pauli-Weisskopf

(1934) In this case the second and the third parts of the self-energy, mentioned above, do not appear at all as the particle has no spin, and the first and last parts diverge quadratically. Following the method of Weisskopf, Richtmyer (1940) worked out the same problem for a particle with spin one assuming the field theory as developed by Proca, Yukawa and others (Proca, 1936, Kemmer, 1938, Frolich, Heitler and Kemmer, 1938, Bhabha, 1938; Yukawa, Sakata and Taketani, 1938, Kobayasi and Okayama, 1939). In this particle the first and the last parts also diverge quadratically, and the second and the third parts separately as  $P^4$ , but the whole self-energy diverges quadratically.

Recently Duffin (1938) and Kemmer (1939) developed the theories of particles with spins one and zero from a single scheme. They derived the equations of these particles in a form which is analogous to Dirac's equation of electron. This formulation of Duffin and Kemmer, as shown by various authors (Booth and Wilson, 1940, Wilson, 1940, Christy and Kusaka, 1941) whose procedure of calculations is similar to that as applied to Dirac's electron, can be used with more advantage in the problems of the interaction between meson and the electromagnetic field than the usual field theory. It may, therefore, be of some interest to work out the problem of the self-energy of meson from the Duffin-Kemmer's formalism following the method of Weisskopf. The advantage of using this formalism is that the results for particles with spins one and zero are obtained from a single scheme; moreover, as the method of calculations is somewhat similar to that as applied to Dirac's electron, these results can be compared in every stage with the corresponding results as obtained by Weisskopf for an electron in the positron theory.

In the first two articles all the necessary equations are given and the method of approximation, which is applied in the Duffin-Kemmer's formalism, is developed. The charge distribution and the static field energy are calculated in the third article, and the electromagnetic field produced by meson and the contribution to the self-energy by the spin are worked out in the fourth one. The part of the self-energy produced by the zero point fluctuations of the radiation field is obtained in the fifth article. By way of check the transverse self-energy is calculated in the last article directly by a second order perturbation calculation.

## 1 EQUATIONS OF MESON THEORY

Kemmer's wave equation for meson in the presence of the electromagnetic field is

$$\left( \frac{\partial}{\partial x_\mu} - \frac{ie}{\hbar c} \phi_\mu \right) \beta_\mu \psi + \kappa \psi = 0 \quad \dots \dots (1)$$

where  $\kappa = \frac{mc}{\hbar}$ ,  $x_4 = ict$ , and the operators  $\beta_\mu$  are hermitian matrices obeying the Duffin's commutation rules

$$\beta_\mu \beta_\nu \beta_\rho + \beta_\mu \beta_\rho \beta_\nu = \beta_\mu \delta_{\nu\rho} + \beta_\nu \delta_{\rho\mu} \quad \dots \dots (2)$$

For meson with spin one  $\beta$ 's are ten-row square matrices and for spinless meson they are five-row ones. The current and charge densities are given by

$$\left. \begin{aligned} i_k &= e\psi^\dagger \beta_k \psi = ie\psi^* \eta_k \beta_k \psi, \\ \rho &= -ie\psi^\dagger \beta_4 \psi = e\psi^* \beta_4 \psi, \end{aligned} \right\} \quad (3)$$

where

$$\psi^\dagger = \psi^* \eta_4, \quad \eta_4 = 2\beta_4^2 - 1 \quad (4)$$

The equation of supplementary condition is given by

$$\left( \frac{\partial}{\partial x_k} - \frac{ie}{\hbar c} \phi_k \right) \beta_k \beta_4^2 \psi + \kappa (1 - \beta_4^2) \psi = 0 \quad (5)$$

with the help of which we can eliminate those components of  $\psi$  for which  $\beta_4 \psi$  is zero and which are not directly quantised. It is to be understood that repeated suffixes mean summation, Greek suffixes run from 1 to 4, and Latin from 1 to 3.

The Hamiltonian function (B & W, eqn 55)<sup>1</sup> is given by

$$H = \int \left[ -i\hbar c \psi^\dagger \beta_k \frac{\partial \psi}{\partial x_k} - e\psi^\dagger \beta_\mu \phi_\mu \psi - imc^2 \psi^\dagger \psi - \frac{1}{4\pi} \phi \operatorname{div} \mathbf{E} + \frac{1}{8\pi} (\mathbf{E}^2 + \mathbf{H}^2) \right] d\mathbf{r}. \quad (6)$$

This Hamiltonian is to be considered subject to the restrictions (5) and

$$\frac{1}{c} \frac{\partial \phi}{\partial t} + \operatorname{div} \mathbf{A} = 0$$

In the ten-components theory, for a given  $\mathbf{p}$ , the equation of the free meson has six linearly independent solutions, viz

$$\phi_k^+(\mathbf{p}) = \frac{1}{\sqrt{V}} u_k^+(\mathbf{p}) \exp \left\{ -\frac{i}{\hbar} E(\mathbf{p})t + \frac{i}{\hbar} (\mathbf{p}\mathbf{r}) \right\} \quad \dots \quad (7)$$

for positively charged states with momentum  $\mathbf{p}$ , and

$$\phi_k^-(\mathbf{p}) = \frac{1}{\sqrt{V}} u_k^-(\mathbf{p}) \exp \left\{ \frac{i}{\hbar} E(\mathbf{p})t + \frac{i}{\hbar} (\mathbf{p}\mathbf{r}) \right\} \quad (8)$$

for negatively charged states with momentum  $-\mathbf{p}$ , where  $k = 1, 2, 3$  correspond to the three states of polarisation which are taken to be transverse and longitudinal to the direction of motion, while the five-components theory has two linearly independent solutions given by (7) and (8), and the polarisation is longitudinal. The equations satisfied by  $u^+(\mathbf{p})$  and  $u^-(\mathbf{p})$  are

$$\{ \mp E(\mathbf{p})\beta_4 + ic(\mathbf{p}\beta) + mc^2 \} u^\pm(\mathbf{p}) = 0 \quad \dots \quad (9)$$

with the equations of condition

$$u^\pm(\mathbf{p}) = \left\{ 1 - \frac{i}{mc} (\mathbf{p}\beta) \right\} \beta_4^2 u^\pm(\mathbf{p}), \quad (10)$$

<sup>1</sup> Henceforth B & W refers to the paper of Booth and Wilson.

and  $u$ 's satisfy the following normalising and orthogonality relations

$$\left. \begin{aligned} mc^2 u_k^* u_l &= E \delta_{kl}, & u_k^{+*} \beta_4 u_l^+ &= \delta_{kl}, \\ u_k^{-*} \beta_4 u_l^- &= -\delta_{kl}, & u_k^{+*} \beta_4 u_l^- &= 0 \end{aligned} \right\} \quad (11)$$

where  $E = c(p^2 + m^2 c^2)^{\frac{1}{2}}$

The wave function  $\psi$  of any system can be expanded in wave functions of free meson as

$$\psi = \sum_p \sum_k \{ a_k(p) \phi_k^+(p) + b_k^*(p) \phi_k^-(p) \} \quad (12)$$

where  $a$ 's and  $b$ 's are  $q$ -numbers and  $u$ 's are column matrices with  $c$ -number components. As in the most of the problems we shall have to take either the sum or the average over different polarisations of meson, we shall for convenience drop the suffix  $k$  and the summation over it. By the method of second quantisation it is well known that the operators  $a$ 's and  $b$ 's satisfy the relations

$$\left. \begin{aligned} a^*(p) a(p) &= N^+(p), & a(p) a^*(p) &= N^+(p) + 1, \\ b^*(p) b(p) &= N^-(p), & b(p) b^*(p) &= N^-(p) + 1, \end{aligned} \right\} \quad (13)$$

where  $N^+(p)$  and  $N^-(p)$  give the number of positive and negative mesons in the state  $p$

## 2 THE METHOD OF APPROXIMATION

The method, used here, is somewhat similar to that as used by Weisskopf. If the components of  $\psi$  for which  $\beta_4 \psi$  is zero are eliminated from (6) by (5), then after partial integration the Hamiltonian can be written in the form

$$H = H_0 + eH' + e^2 H'', \quad (14)$$

where

$$\begin{aligned} H_0 &= \int \left[ mc^2 \psi^* \beta_4 \psi + \frac{\hbar^2}{m} \frac{\partial \psi^*}{\partial x_k} \beta_4^2 \beta_k \beta_4 \frac{\partial \psi}{\partial x_l} - \frac{1}{4\pi} \phi \operatorname{div} \mathbf{E} + \frac{1}{8\pi} (\mathbf{E}^2 + \mathbf{H}^2) \right] dx, \\ H' &= -\frac{i\hbar}{mc} \int \left[ \frac{\partial \psi^*}{\partial x_k} \beta_4^2 \beta_k (\beta_4 \mathbf{A}) \beta_4^2 \psi - \psi^* \beta_4^2 (\beta_4 \mathbf{A}) \beta_k \beta_4^2 \frac{\partial \psi}{\partial x_k} \right] dx + \int \psi^* \beta_4 \psi \phi dx, \quad (15) \end{aligned}$$

$$H'' = \frac{1}{mc^2} \int \psi^* \beta_4^2 (\beta_4 \mathbf{A})^2 \beta_4^2 \psi dx \quad (16)$$

The terms  $eH'$  and  $e^2 H''$  give the interaction energy between the matter and the field. The operator  $H$  depends explicitly on  $e$  as shown in (14), where  $H_0$ ,  $H'$  and  $H''$  are explicitly independent of  $e$ . If  $e$  is increased by  $de$ , the Hamiltonian acquires the additional term  $H' de + 2H'' e de$ , and according to the perturbation theory the energy of the stationary state  $s$  of the Hamiltonian is increased by

$$dW' = (H'(e))_{\Delta V} de + 2(H''(e))_{\Delta V} e de,$$

where  $(H'(e))_{AV}$  and  $(H''(e))_{AV}$  are the time average of  $H'$  and  $H''$  respectively in the state  $s$  with the initial charge  $e$ . Hence the total increase of energy when the charge is increased from zero to  $e$  is given by

$$W' = \int_0^e [(H'(e))_{AV} + 2(H''(e))_{AV} e] de \quad (17)$$

which would, of course, give the self-energy of meson. For approximation we expand  $H'(e)$  and  $H''(e)$  as

$$H'(e) = b_0 + b_1 e + b_2 e^2 + \dots,$$

$$H''(e) = c_0 + c_1 e + c_2 e^2 + \dots,$$

and from (17) we get

$$W' = e(b_0)_{AV} + \frac{e^2}{2}(b_1)_{AV} + \frac{e^3}{3}(b_2)_{AV} + e^2(c_0)_{AV} + \frac{2e^3}{3}(c_1)_{AV} + \dots$$

Since the self-energy cannot depend on the sign of  $e$ , the coefficients of all the odd powers of  $e$  must be zero, and we have approximately

$$W' = \frac{e^2}{2}(b_1)_{AV} + e^2(c_0)_{AV} \sim \frac{1}{2} \{eH'(e) + 2e^2H''(e)\}_{AV} \quad (18)$$

Again if the unwanted components of  $\psi$  for which  $\beta_4\psi = 0$  are eliminated by (5) from the expression of current as given by (3), we get

$$i = i_1 + i_2 \quad (19)$$

where

$$i_1 = \frac{ie\hbar}{mc} \left\{ \frac{\partial\psi^*}{\partial x_k} \beta_4^2 \beta_k \beta_4^2 \psi - \psi^* \beta_4^2 \beta_k \beta_4^2 \frac{\partial\psi}{\partial x_k} \right\}, \quad (20)$$

$$i_2 = -\frac{e^2}{mc^2} \psi^* \beta_4^2 \{ \beta(\beta A) + (\beta A)\beta \} \beta_4^2 \psi \quad (21)$$

Hence considering (15) and (16), (18) reduces to

$$W' = \frac{1}{2} \int \{ (\rho\phi)_{AV} - (iA)_{AV} \} d\mathbf{r} \quad (22)$$

In this expression we write

$$A = A_0 + A', \quad \phi = \phi' \quad (23)$$

where  $A'$  and  $\phi'$  is the field generated by the meson, and  $A_0$  is the potential for  $e = 0$ , that is of the zero point field. Using Maxwell's field equations through which  $i$  and  $\rho$  are connected with  $A'$  and  $\phi'$ , we partially eliminate  $i$  and  $\rho$  from (22). Then on partial integrations with respect to space co-

ordinates as well as with respect to time (which is justified since the diagonal elements are the time average) we obtain

$$W' = \frac{1}{8\pi} \int \{ (\mathbf{E}'^2)_{AV} - (\mathbf{H}'^2)_{AV} \} d\mathbf{r} - \frac{1}{2} \int (i\mathbf{A}_0)_{AV} d\mathbf{r} \quad (24)$$

We split the electric field  $\mathbf{E}'$  into longitudinal part  $\mathbf{E}_{\text{long}}$  and transverse part  $\mathbf{E}'_{\text{tr}}$ . The former gives the static field energy

$$W_{\text{st}} = \frac{1}{8\pi} \int (\mathbf{E}_{\text{long}}^2)_{AV} d\mathbf{r} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (25)$$

Then

$$W' = W_{\text{st}} + W_{\text{tr}}$$

where  $W_{\text{tr}}$  is the transverse self-energy and is given by

$$\begin{aligned} W_{\text{tr}} &= \frac{1}{8\pi} \int (\mathbf{E}_{\text{tr}}^2)_{AV} d\mathbf{r} - \frac{1}{8\pi} \int (\mathbf{H}^2)_{AV} d\mathbf{r} - \frac{1}{2} \int (i\mathbf{A}_0)_{AV} d\mathbf{r} \\ &= U_{\text{el}} - U_{\text{mag}} + W_{\text{fluct}} \end{aligned} \quad (26)$$

in the notation of Weisskopf  $W_{\text{fluct}}$  is the energy due to the zero point fluctuations of the radiation field

### 3 THE CHARGE DISTRIBUTION AND ELECTROSTATIC FIELD ENERGY OF MESON

The commutation rule (B & W, eqn 32) for components of  $\psi$  for which  $\beta_4\psi$  is not zero is given by

$$\{ \beta_4\psi(\mathbf{r}') \}_\sigma \{ \psi^*(\mathbf{r})\beta_4^2 \}_\rho - \{ \psi^*(\mathbf{r})\beta_4^2 \}_\rho \{ \beta_4\psi(\mathbf{r}') \}_\sigma = \delta_{\rho\sigma} \delta(\mathbf{r} - \mathbf{r}') \quad (27)$$

Then following Heisenberg's rule (1934), we replace the charge density  $e\psi^*\beta_4\psi$  by

$$\rho = \frac{1}{2} e \{ \psi^*\beta_4\psi + \beta_4\psi \psi^*\beta_4^2 \} \quad (28)$$

with this the total charge in a volume  $V$  is given by

$$\int \rho(\mathbf{r}) d\mathbf{r} = e \sum_{\mathbf{p}} [N^+(\mathbf{p}) - N^-(\mathbf{p})] \quad \dots \quad (29)$$

Thus the choice of (28) avoids the total zero point charge in the vacuum of the meson theory, and this result is consistent with that given by Pauli (1941). (28) may then be considered as the effective charge density of a system of particles.

We now construct a function

$$G(\xi) = \int \rho(\mathbf{r}_2)\rho(\mathbf{r}_1) d\mathbf{r} \quad \dots \quad (30)$$

where  $\rho(\mathbf{r})$  is given by (28), and  $\mathbf{r}_1 = \mathbf{r} - \boldsymbol{\xi}/2$ ,  $\mathbf{r}_2 = \mathbf{r} + \boldsymbol{\xi}/2$ . This function gives us information about the charge distribution in the neighbourhood of meson. In the language of the electron theory, the probability<sup>1</sup> of finding the charge simultaneously at two points in a distance  $\boldsymbol{\xi}$  is given by  $G(\boldsymbol{\xi})$ . We substitute (12) in (30) and retain those terms which have the time average, that is, those terms which contribute to the expectation value  $\bar{G}(\boldsymbol{\xi})$ . Then by (11) and (13) we obtain

$$\begin{aligned} \bar{G}(\boldsymbol{\xi}) = & \frac{e^2}{V} \sum_{\mathbf{p}} \sum_{\mathbf{p}'} [N^+(\mathbf{p})N^+(\mathbf{p}') - 2N^+(\mathbf{p})N^-(\mathbf{p}') + N^-(\mathbf{p})N^-(\mathbf{p}')] \\ & + e^2 \sum_{\mathbf{p}} \sum_{\mathbf{p}'} \int [N^+(\mathbf{p})(N^+(\mathbf{p}') + 1) \{ \phi^+(\mathbf{p}, \mathbf{r}_2)^* \beta_4 \phi^+(\mathbf{p}', \mathbf{r}_2) \} \{ \phi^+(\mathbf{p}', \mathbf{r}_1)^* \beta_4 \phi^+(\mathbf{p}, \mathbf{r}_1) \} \\ & + (N^-(\mathbf{p}) + 1)N^-(\mathbf{p}') \{ \phi^-(\mathbf{p}, \mathbf{r}_2)^* \beta_4 \phi^-(\mathbf{p}', \mathbf{r}_2) \} \{ \phi^-(\mathbf{p}', \mathbf{r}_1)^* \beta_4 \phi^-(\mathbf{p}, \mathbf{r}_1) \} \\ & + N^+(\mathbf{p})N^-(\mathbf{p}') \{ \phi^+(\mathbf{p}, \mathbf{r}_2)^* \beta_4 \phi^-(\mathbf{p}', \mathbf{r}_2) \} \{ \phi^-(\mathbf{p}', \mathbf{r}_1)^* \beta_4 \phi^+(\mathbf{p}, \mathbf{r}_1) \} \\ & + (N^-(\mathbf{p}) + 1)(N^+(\mathbf{p}') + 1) \{ \phi^-(\mathbf{p}, \mathbf{r}_2)^* \beta_4 \phi^+(\mathbf{p}', \mathbf{r}_2) \} \{ \phi^+(\mathbf{p}', \mathbf{r}_1)^* \beta_4 \phi^-(\mathbf{p}, \mathbf{r}_1) \}] d\mathbf{r} \end{aligned} \quad (31)$$

where  $\phi^+(\mathbf{p})$  and  $\phi^-(\mathbf{p})$  are given by (7) and (8) respectively. This expression does not vanish for the vacuum where  $N^+(\mathbf{p}) = N^-(\mathbf{p}) = 0$  for all values of  $\mathbf{p}$ , and we have

$$\bar{G}(\boldsymbol{\xi})_{\text{vac}} = e^2 \sum_{\mathbf{p}} \sum_{\mathbf{p}'} \int [ \{ \phi^-(\mathbf{p}, \mathbf{r}_2)^* \beta_4 \phi^+(\mathbf{p}', \mathbf{r}_2) \} \{ \phi^+(\mathbf{p}', \mathbf{r}_1)^* \beta_4 \phi^-(\mathbf{p}, \mathbf{r}_1) \} ] d\mathbf{r}$$

which is infinite. As we are interested in the behaviour of a single meson only, we shall not make further discussion on the nature of this function in the present paper. For definiteness we shall consider the case of positive meson in our subsequent discussion, but our final results will also be valid for negative meson. We consider the single positive meson at rest in the state  $\mathbf{p} = 0$ . If we now put  $N^+(0) = 1$  and all other  $N^+(\mathbf{p} \neq 0) = N^-(\mathbf{p}) = 0$  in (31), the value of  $\bar{G}(\boldsymbol{\xi})_{\text{vac}+1}$  for a single positive meson at rest in the vacuum is obtained, and by subtracting from it the contribution of the vacuum  $\bar{G}(\boldsymbol{\xi})_{\text{vac}}$  we get for a single positive meson only

$$\begin{aligned} \bar{G}(\boldsymbol{\xi}) = & \bar{G}(\boldsymbol{\xi})_{\text{vac}+1} - \bar{G}(\boldsymbol{\xi})_{\text{vac}} \\ = & \frac{2e^2}{V} + e^2 \sum_{\mathbf{p}} \int [ \{ \phi^+(0, \mathbf{r}_2)^* \beta_4 \phi^+(\mathbf{p}, \mathbf{r}_2) \} \{ \phi^+(\mathbf{p}, \mathbf{r}_1)^* \beta_4 \phi^+(0, \mathbf{r}_1) \} \\ & + \{ \phi^+(0, \mathbf{r}_2)^* \beta_4 \phi^-(\mathbf{p}, \mathbf{r}_2) \} \{ \phi^-(\mathbf{p}, \mathbf{r}_1)^* \beta_4 \phi^+(0, \mathbf{r}_1) \} ] d\mathbf{r}. \end{aligned}$$

<sup>1</sup> The charge distribution is essentially a positive quantity in the non-relativistic Schrödinger theory as well as in the Dirac's relativistic electron theory and it can be defined as the probability distribution. In the relativistic theory of Bose particles the charge densities are not positive definite, and serious difficulties arise in this interpretation for then the concept of negative probability comes in. Recently Dirac (Bakerian Lecture, 1942) has suggested some ways of modifying this interpretation.

The first term in this expression is to be omitted, because this term becomes zero for  $V \rightarrow \infty$ . Hence by (7) and (8)

$$\bar{G}(\xi) = \frac{e^2}{V} \sum_p \left[ \{ u^+(0) \beta_4 u^+(\mathbf{p}) \} \{ u^+(\mathbf{p}) \beta_4 u^+(0) \} \right. \\ \left. + \{ u^+(0) \beta_4 u^-(\mathbf{p}) \} \{ u^-(\mathbf{p}) \beta_4 u^+(0) \} \right] e^{\frac{i}{\hbar}(\mathbf{p}\xi)} \quad (32)$$

For a meson with spin one ( $10 \times 10$  matrices) there are three directions of polarisation over which the summation is to be taken in the state  $\mathbf{p}$ . This summation is performed by using the relations

$$\left. \begin{aligned} \sum_{k=1}^3 \beta_4^2 \{ u_k^+(\mathbf{p}) u_k^+(\mathbf{p})^* - u_k^-(\mathbf{p}) u_k^-(\mathbf{p})^* \} \beta_4^2 &= \beta_4, \\ \sum_{k=1}^3 \beta_4^2 \{ u_k^+(\mathbf{p}) u_k^+(\mathbf{p})^* + u_k^-(\mathbf{p}) u_k^-(\mathbf{p})^* \} \beta_4^2 &= \frac{mc^2}{E(\mathbf{p})} \beta_4 \left[ 1 + \frac{1}{m^2 c^2} (\mathbf{p}\beta)^2 \right] \beta_4 \end{aligned} \right\} \quad (33)$$

Again we shall have to average over the directions of polarisation in the state  $\mathbf{p} = 0$ . For this purpose we sum over the three directions of polarisation and divide by 3. This summation is to be performed by introducing the annihilation operator (B & W, eqn 107), which is obtained from (9) and (10),

$$\left. \begin{aligned} \frac{1}{2E(\mathbf{p})} \left[ E(\mathbf{p}) \beta_4 + mc^2 + \frac{1}{m} (\mathbf{p}\beta)^2 \right] \beta_4^2 u^+(\mathbf{p}) &= \beta_4 u^+(\mathbf{p}), \\ \frac{1}{2E(\mathbf{p})} \left[ E(\mathbf{p}) \beta_4 + mc^2 + \frac{1}{m} (\mathbf{p}\beta)^2 \right] \beta_4^2 u^-(\mathbf{p}) &= 0 \end{aligned} \right\} \quad (34)$$

On performing the above operations, (32) assumes the form

$$\bar{G}(\xi) = \frac{e^2 mc^2}{6V} \sum_p \frac{1}{E(\mathbf{p})} e^{\frac{i}{\hbar}(\mathbf{p}\xi)} \text{spur } \beta_4 \left[ 1 + \frac{1}{m^2 c^2} (\mathbf{p}\beta)^2 \right] (\beta_4^2 + \beta_4) \quad (35)$$

For meson with spin zero ( $5 \times 5$  matrices) calculations are the same; the only difference from the particle with spin one is that the factor  $\frac{1}{3}$  must be omitted

The factor  $\frac{1}{3}$  arises because of the averaging over the three polarisations; for spinless particles averaging is unnecessary since there is only one polarisation. Spur calculations, the detail method of which is given by Booth and Wilson, are also somewhat different

On evaluating the spurs we obtain for both the particles (mesons with spins one and zero) at rest after replacing the sum over the states by an integral over the momenta of the states

$$\bar{G}(\xi) = \frac{e^2 mc^2}{2(2\pi\hbar)^3} \int \frac{d\mathbf{p}}{E(\mathbf{p})} \left( 2 + \frac{p^2}{m^2 c^2} \right) e^{\frac{i}{\hbar}(\mathbf{p}\xi)} \quad (36)$$

which gives

$$\bar{G}(\xi) = e^2 \frac{mc}{\hbar} \frac{1}{8\pi i} \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( 2 - \frac{\hbar^2}{m^2 c^2} \frac{\partial^2}{\partial \xi^2} \right) H_0^1 \left( i \frac{mc}{\hbar} \xi \right) \quad (37)$$

where  $H_0^1(z)$  is the Hankel function of the first kind which has a logarithmic singularity for  $|z| = 0$  and decreases exponentially for  $|z| \gg 1$ . The expression (37) varies as  $\frac{1}{\xi^4}$  for  $\xi \ll \frac{\hbar}{mc}$  and falls off exponentially for  $\xi \gg \frac{\hbar}{mc}$ ,

and so shows a spread of charge over a finite region of the order of  $\frac{\hbar}{mc}$ . In the case of the electron in the positron theory, as shown by Weisskopf,  $\bar{G}(\xi)$  varies as  $\frac{1}{\xi^2}$  for  $\xi \ll \frac{\hbar}{mc}$ . Hence in the meson theory the charge distribution has a higher order singularity than that in the positron theory. This result is quite consistent with what is to be expected for in the case of particles obeying Bose statistics the probability of two like particles being closer than their wave-lengths is larger than that at longer distances. This higher order singularity in the charge distribution is much reflected on the electrostatic self-energy which will be shown presently.

The electrostatic energy  $W_{st}$  is given by (25) and can be written as

$$W_{st} = \frac{1}{2} \iint \frac{\rho(\mathbf{r} + \xi/2) \rho(\mathbf{r} - \xi/2)}{|\xi|} d\mathbf{r} d\xi = \frac{1}{2} \int \frac{\bar{G}(\xi)}{|\xi|} d\xi$$

where  $\bar{G}(\xi)$  is given by (36). On evaluating the integration over  $\xi$  first, we obtain, in terms of the 'cut off momentum'  $P$  which is the greatest value we allow for  $p$ ,

$$\begin{aligned} W_{st} &= \frac{e^2}{8\pi^2 \hbar mc} \int dp \cdot \frac{p^2 + 2m^2 c^2}{p^2 \sqrt{p^2 + m^2 c^2}} \\ &= \frac{e^2}{4\pi \hbar mc} \lim_{P \rightarrow \infty} \left[ P \sqrt{P^2 + m^2 c^2} + 3m^2 c^2 \log \frac{P + \sqrt{P^2 + m^2 c^2}}{mc} \right] \end{aligned} \quad (38)$$

Putting  $\frac{\hbar}{P} = a$ , where  $a$  is the 'cut off radius', we have

$$\begin{aligned} W_{st} &= \frac{e^2 \kappa}{12\pi} \lim_{P \rightarrow \infty} \left[ 3 \left( \frac{P}{mc} \right)^2 + 9 \log \left( \frac{P}{mc} \right) \right] + \text{finite terms} \\ &= \frac{e^2 \kappa}{12\pi} \lim_{a \rightarrow 0} \left[ 3 \left( \frac{\hbar}{mca} \right)^2 + 9 \log \left( \frac{\hbar}{mca} \right) \right] + \text{finite terms.} \end{aligned} \quad (39)$$

Thus the singularity of the order of  $\frac{1}{\xi^4}$  in  $\bar{G}(\xi)$  causes the quadratic divergence of  $W_{st}$ , whereas for an electron in the positron theory this divergence is logarithmic produced by the quadratic singularity of  $\bar{G}(\xi)$ .

## 4 THE ELECTROMAGNETIC FIELD OF MESON

The vector potential  $\mathbf{A}'$  of the electromagnetic field produced by meson is given by

$$\mathbf{A}'(\mathbf{r}, t) = \int \frac{\mathbf{j}(\mathbf{r}', t')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

where  $t' = t - \frac{|\mathbf{r} - \mathbf{r}'|}{c}$ , and the current density  $\mathbf{j}$  is given by (3). In the order of approximation we are interested we consider  $\psi$  to be the solutions of the equations of free meson. Then expanding  $\psi$  according to (12) and considering (7) and (8) we obtain after some calculations

$$\begin{aligned} \mathbf{A}'(\mathbf{r}, t) = & \frac{2\pi i e \hbar^2 c^2}{V} \sum_p \sum_p \left[ \{E(\mathbf{p})E(\mathbf{p}') - m^2 c^4 - c^2(\mathbf{p}\mathbf{p}')\}^{-1} \right. \\ & \times \left\{ a^*(\mathbf{p})a(\mathbf{p}')u^+(\mathbf{p})^* \eta_4 \beta u^+(\mathbf{p}') \exp - \frac{i}{\hbar} (E(\mathbf{p}') - E(\mathbf{p}))t \right. \\ & + b(\mathbf{p})b^*(\mathbf{p}')u^-(\mathbf{p})^* \eta_4 \beta u^-(\mathbf{p}') \exp \frac{i}{\hbar} (E(\mathbf{p}') - E(\mathbf{p}))t \} - \{E(\mathbf{p})E(\mathbf{p}') + m^2 c^4 \\ & + c^2(\mathbf{p}\mathbf{p}')\}^{-1} \left\{ a^*(\mathbf{p})b^*(\mathbf{p}')u^+(\mathbf{p})^* \eta_4 \beta u^-(\mathbf{p}') \exp \frac{i}{\hbar} (E(\mathbf{p}') + E(\mathbf{p}))t \right. \\ & \left. \left. + b(\mathbf{p})a(\mathbf{p}')u^-(\mathbf{p})^* \eta_4 \beta u^+(\mathbf{p}') \exp - \frac{i}{\hbar} (E(\mathbf{p}') + E(\mathbf{p}))t \right\} \right] \exp \frac{i}{\hbar} (\mathbf{p}' - \mathbf{p}, \mathbf{r}) \quad (40) \end{aligned}$$

Hence the magnetic field  $\mathbf{H}'$  is given by

$$\begin{aligned} \mathbf{H}' = \text{rot } \mathbf{A}' = & - \frac{2\pi e \hbar c^2}{V} \sum_p \sum_p \left[ \{E(\mathbf{p})E(\mathbf{p}') - m^2 c^4 - c^2(\mathbf{p}\mathbf{p}')\}^{-1} \right. \\ & \times \left\{ a^*(\mathbf{p})a(\mathbf{p}')u^+(\mathbf{p})^* \eta_4 \beta_s u^+(\mathbf{p}') \exp - \frac{i}{\hbar} (E(\mathbf{p}') - E(\mathbf{p}))t \right. \\ & + b(\mathbf{p})b^*(\mathbf{p}')u^-(\mathbf{p})^* \eta_4 \beta_s u^-(\mathbf{p}') \exp \frac{i}{\hbar} (E(\mathbf{p}') - E(\mathbf{p}))t \} - \{E(\mathbf{p})E(\mathbf{p}') + m^2 c^4 \\ & + c^2(\mathbf{p}\mathbf{p}')\}^{-1} \left\{ a^*(\mathbf{p})b^*(\mathbf{p}')u^+(\mathbf{p})^* \eta_4 \beta_s u^-(\mathbf{p}') \exp \frac{i}{\hbar} (E(\mathbf{p}') + E(\mathbf{p}))t \right. \\ & \left. \left. + b(\mathbf{p})a(\mathbf{p}')u^-(\mathbf{p})^* \eta_4 \beta_s u^+(\mathbf{p}') \exp - \frac{i}{\hbar} (E(\mathbf{p}') + E(\mathbf{p}))t \right\} \right] \\ & \times |\mathbf{p} - \mathbf{p}'| \exp \frac{i}{\hbar} (\mathbf{p}' - \mathbf{p}, \mathbf{r}) \quad (41) \end{aligned}$$

where  $\beta_s, |\mathbf{p} - \mathbf{p}'| = [\beta, \mathbf{p} - \mathbf{p}']$ , that is,  $\beta_s$  is the projection of  $\beta$  perpendicular to  $\mathbf{p} - \mathbf{p}'$ . Again the transverse part of the electric field is given by

$$\mathbf{E}'_{\text{tr}} = - \frac{1}{c} \frac{\partial \mathbf{A}'_{\text{tr}}}{\partial t}$$

where  $\mathbf{A}'_{tr}$  is the transverse part of  $\mathbf{A}'$ . Then by (40)

$$\begin{aligned} \mathbf{E}'_{tr} = & -\frac{2\pi e\hbar c}{V} \sum_p \sum_{p'} \left[ \frac{E(p') - E(p)}{E(p)E(p') - m^2c^4 - c^2(\mathbf{p}\mathbf{p}')} \right. \\ & \times \left\{ a^*(\mathbf{p})a(p')u^+(\mathbf{p})^*\eta_4\beta_4u^+(p') \exp -\frac{i}{\hbar}(E(p') - E(p))t \right. \\ & - b(\mathbf{p})b^*(p')u^-(\mathbf{p})^*\eta_4\beta_4u^-(p') \exp \frac{i}{\hbar}(E(p') - E(p))t \left. \right\} + \frac{E(p') + E(p)}{E(p)E(p') + m^2c^4 + c^2(\mathbf{p}\mathbf{p}')} \\ & \times \left\{ a^*(\mathbf{p})b^*(p')u^+(\mathbf{p})^*\eta_4\beta_4u^-(p') \exp \frac{i}{\hbar}(E(p') + E(p))t \right. \\ & \left. - b(\mathbf{p})a(p')u^-(\mathbf{p})^*\eta_4\beta_4u^+(\mathbf{p}') \exp -\frac{i}{\hbar}(E(p') + E(p))t \right\} \left. \right] \exp \frac{i}{\hbar}(\mathbf{p}' - \mathbf{p}, \mathbf{r}) \quad (42) \end{aligned}$$

It is evident that  $\text{div } \mathbf{E}'_{tr} = 0$  is satisfied, since  $(\beta_4, \mathbf{p}' - \mathbf{p}) = 0$

*Magnetic field energy*—In order to evaluate the time average of the magnetic field energy

$$\frac{1}{8\pi} \int |\mathbf{H}'|^2 d\mathbf{r}$$

we shall have to substitute (41), and retain only the diagonal elements. In consequence of the relations (13) we have then

$$\begin{aligned} U_{\text{mag}} = & \frac{\pi e^2 \hbar^2 c^4}{2V} \sum_p \sum_{p'} |\mathbf{p} - \mathbf{p}'|^2 \left[ \{E(p)E(p') - m^2c^4 - c^2(\mathbf{p}\mathbf{p}')\}^{-2} \right. \\ & \times \{N^+(\mathbf{p})(N^+(\mathbf{p}') + 1)\{u^+(\mathbf{p})^*\eta_4\beta_4u^+(p')\}\{u^+(p')^*\beta_4\eta_4u^+(\mathbf{p})\} \\ & + (N^-(\mathbf{p}) + 1)N^-(p')\{u^-(\mathbf{p})^*\eta_4\beta_4u^-(p')\}\{u^-(p')^*\beta_4\eta_4u^-(\mathbf{p})\}\} + \{E(p)E(p') \\ & + m^2c^4 + c^2(\mathbf{p}\mathbf{p}')\}^{-2} \{N^+(\mathbf{p})N^-(p')\{u^+(\mathbf{p})^*\eta_4\beta_4u^-(p')\}\{u^-(p')^*\beta_4\eta_4u^+(\mathbf{p})\} \\ & \left. + (N^-(\mathbf{p}) + 1)(N^+(p') + 1)\{u^-(\mathbf{p})^*\eta_4\beta_4u^+(p')\}\{u^+(p')^*\beta_4\eta_4u^-(\mathbf{p})\}\} \right] \quad (43) \end{aligned}$$

If we now calculate  $U_{\text{mag}}$  for vacuum by putting  $N^+(\mathbf{p}) = N^-(\mathbf{p}) = 0$  for all  $\mathbf{p}$ , we get an expression which is highly divergent. This highly divergent magnetic field energy  $U_{\text{mag}}(\text{vac})$  is produced by the current fluctuations of the vacuum. As we are interested only in the magnetic field energy of a single meson at rest ( $\mathbf{p} = 0$ ), we first calculate  $U_{\text{mag}}(\text{vac} + 1)$  by putting  $N^+(0) = 1$ , and all other  $N^+(\mathbf{p} \neq 0) = N^-(\mathbf{p}) = 0$ , and subtract the contribution of the vacuum  $U_{\text{mag}}(\text{vac})$ . Then for a single positive meson at rest

$$\begin{aligned} U_{\text{mag}} = & U_{\text{mag}}(\text{vac} + 1) - U_{\text{mag}}(\text{vac}) \\ = & \frac{\pi e^2 \hbar^2}{2Vm^2} \sum_p |\mathbf{p}|^2 \left[ \frac{\{u^+(0)^*\eta_4\beta_4u^+(\mathbf{p})\}\{u^+(\mathbf{p})^*\beta_4\eta_4u^+(0)\}}{\{E(\mathbf{p}) - mc^2\}^2} \right. \\ & \left. + \frac{\{u^+(0)^*\eta_4\beta_4u^-(\mathbf{p})\}\{u^-(\mathbf{p})^*\beta_4\eta_4u^+(0)\}}{\{E(\mathbf{p}) + mc^2\}^2} \right] \end{aligned}$$

Eliminating by (10) the components of  $u^\pm$  for which  $\beta_4 u^\pm = 0$ , we as before sum over the directions of polarisation in the state  $\mathbf{p}$  and average over that of the state  $\mathbf{p} = 0$ , and obtain for a meson with spin one

$$U_{\text{mag}} = \frac{\pi e^2 \hbar^2}{12 V m^3 c^2} \sum_{\mathbf{p}} \frac{1}{p^2 E(\mathbf{p})} (p^2 + 2m^2 c^2) \text{spur } \beta_4 \beta_s (\mathbf{p} \beta) \beta_s^2 (\mathbf{p} \beta) \beta_s (\beta_4^2 + \beta_4),$$

and for spinless meson the factor  $\frac{1}{3}$  will be absent. On evaluating the spurs in both the cases, we get for a meson with spin zero

$$U_{\text{mag}} = 0, \quad (44)$$

and for a meson with spin one

$$\begin{aligned} U_{\text{mag}} &= \frac{\pi e^2 \hbar^2}{3 V m^3 c^2} \sum_{\mathbf{p}} \frac{p^2 + 2m^2 c^2}{E(\mathbf{p})} = \frac{\pi e^2 \hbar^2}{3 m^3 c^2} \frac{1}{(2\pi \hbar)^3} \int d\mathbf{p} \frac{p^2 + 2m^2 c^2}{\sqrt{p^2 + m^2 c^2}} \\ &= \frac{e^2 \kappa}{12\pi} \lim_{P \rightarrow \infty} \left[ \frac{P^3 \sqrt{P^2 + m^2 c^2}}{2m^4 c^4} + \frac{5}{4} \frac{P \sqrt{P^2 + m^2 c^2}}{m^3 c^2} - \frac{5}{4} \log \frac{P + \sqrt{P^2 + m^2 c^2}}{mc} \right] \end{aligned} \quad (45a)$$

$$= \frac{e^2 \kappa}{12\pi} \lim_{P \rightarrow \infty} \left[ \frac{1}{2} \left( \frac{P}{mc} \right)^4 + \frac{3}{2} \left( \frac{P}{mc} \right)^2 - \frac{5}{4} \log \left( \frac{P}{mc} \right) \right] + \text{finite terms} \quad (45b)$$

which diverges as  $P^4$

*Transverse electric field energy*—On performing the calculations as in the previous cases, the time average of the transverse electric field energy is given by (42) as

$$\begin{aligned} U_{\text{el}} &= \frac{1}{8\pi} \int (|\mathbf{E}'_{\text{tr}}|^2)_{A \vee} d\mathbf{r} \\ &= \frac{\pi e^2 \hbar^2 c^2}{2V} \sum_{\mathbf{p}} \sum_{\mathbf{p}'} \left[ \frac{\{E(\mathbf{p}') - E(\mathbf{p})\}^2}{\{E(\mathbf{p})E(\mathbf{p}') - m^2 c^4 - c^2(\mathbf{p} \mathbf{p}')\}^2} \{N^+(\mathbf{p})(N^+(\mathbf{p}') + 1) \right. \\ &\quad \times \{u^+(\mathbf{p})^* \eta_4 \beta_s u^+(\mathbf{p}')\} \{u^+(\mathbf{p}')^* \beta_s \eta_4 u^+(\mathbf{p})\} \\ &\quad + (N^-(\mathbf{p}) + 1) N^-(\mathbf{p}') \{u^-(\mathbf{p})^* \eta_4 \beta_s u^-(\mathbf{p}')\} \cdot \{u^-(\mathbf{p}')^* \beta_s \eta_4 u^-(\mathbf{p})\} \} \\ &\quad + \frac{\{E(\mathbf{p}') + E(\mathbf{p})\}^2}{\{E(\mathbf{p})E(\mathbf{p}') + m^2 c^4 + c^2(\mathbf{p} \mathbf{p}')\}^2} \\ &\quad \times \{N^+(\mathbf{p}) N^-(\mathbf{p}') \{u^+(\mathbf{p})^* \eta_4 \beta_s u^-(\mathbf{p}')\} \{u^-(\mathbf{p}')^* \beta_s \eta_4 u^+(\mathbf{p})\} \\ &\quad \left. + (N^-(\mathbf{p}) + 1)(N^+(\mathbf{p}') + 1) \{u^-(\mathbf{p})^* \eta_4 \beta_s u^+(\mathbf{p}')\} \cdot \{u^+(\mathbf{p}')^* \beta_s \eta_4 u^-(\mathbf{p})\} \} \right] \end{aligned} \quad (46)$$

When applied to a single positive meson at rest this gives

$$U_{el} = U_{el}(\text{vac} + 1) - U_{el}(\text{vac}) \\ = \frac{\pi e^2 \hbar^2}{2V m^2 c^2} \sum_p \left[ \{u^+(0)^* \eta_4 \beta_s u^+(\mathbf{p})\} \{u^+(\mathbf{p})^* \beta_s \eta_4 u^+(0)\} \right. \\ \left. + \{u^+(0)^* \eta_4 \beta_s u^-(\mathbf{p})\} \{u^-(\mathbf{p})^* \beta_s \eta_4 u^+(0)\} \right],$$

and we then get for a spinless meson

$$U_{el} = 0, \quad (47)$$

and for a meson with spin one

$$U_{el} = \frac{\pi e^2 \hbar^2}{3V m^2 c^2} \sum_p \frac{p^2}{E(\mathbf{p})} = \frac{\pi e^2 \hbar^2}{3m^2 c^2} \frac{1}{(2\pi\hbar)^3} \int d\mathbf{p} \frac{p^2}{\sqrt{p^2 + m^2 c^2}} \\ = \frac{e^2 \kappa}{12\pi} \lim_{P \rightarrow \infty} \left[ \frac{P^3 \sqrt{P^2 + m^2 c^2}}{2m^4 c^4} - \frac{3}{4} \frac{P \sqrt{P^2 + m^2 c^2}}{m^2 c^2} + \frac{3}{4} \log \frac{P + \sqrt{P^2 + m^2 c^2}}{mc} \right] \quad (48a)$$

$$= \frac{e^2 \kappa}{12\pi} \lim_{P \rightarrow \infty} \left[ \frac{1}{2} \left( \frac{P}{mc} \right)^4 - \frac{1}{2} \left( \frac{P}{mc} \right)^2 + \frac{3}{4} \log \left( \frac{P}{mc} \right) \right] + \text{finite terms} \quad (48b)$$

which diverges also as  $P^4$

Thus for a meson with spin one

$$W_{sp} = U_{el} - U_{mag} \\ = \frac{e^2 \kappa}{6\pi} \lim_{P \rightarrow \infty} \left[ -\frac{P \sqrt{P^2 + m^2 c^2}}{m^2 c^2} + \log \frac{P + \sqrt{P^2 + m^2 c^2}}{mc} \right] \quad (49) \\ = \frac{e^2 \kappa}{6\pi} \lim_{P \rightarrow \infty} \left[ -\left( \frac{P}{mc} \right)^2 + \log \left( \frac{P}{mc} \right) \right] + \text{finite terms},$$

but for a spinless meson this quantity is zero. Hence  $W_{sp}$  which diverges quadratically, may be considered as a contribution to the self-energy of meson at rest due to spin only. In the case of an electron in the positron theory both  $U_{el}$  and  $U_{mag}$  diverge quadratically, and so also  $W_{sp}$ .

### 5 ENERGY DUE TO THE FLUCTUATIONS OF THE RADIATION FIELD

It has already been shown that

$$\mathbf{i} = \mathbf{i}_1 + \mathbf{i}_2$$

where  $\mathbf{i}_1$  and  $\mathbf{i}_2$  are given by (20) and (21) respectively. Then by (26)

$$W_{\text{fluct}} = W_{\text{fluct}}^1 + W_{\text{fluct}}^2 \\ = -\frac{1}{2} \int (\mathbf{i}_1 \mathbf{A}_0)_{AV} d\mathbf{r} - \frac{1}{2} \int (\mathbf{i}_2 \mathbf{A}_0)_{AV} d\mathbf{r} \quad (50)$$

where  $\mathbf{A}_0$  is the vector potential of the zero-point radiation field. In (21)  $\mathbf{i}_2$  is proportional to  $e^2$ , so in order to get a result to the desired degree of approximation,  $\psi$  in  $\mathbf{i}_2$  can be replaced by unperturbed wave functions. Hence introducing (12) and retaining only the diagonal elements, we get

$$\begin{aligned} W_{\text{fluct}}^2 &= -\frac{1}{2} \int (\mathbf{i}_2 \mathbf{A}_0) d\mathbf{r} = \frac{e^2}{mc^2} \int \psi^* \beta_4^2 (\beta \mathbf{A}_0)^2 \beta_4^2 \psi d\mathbf{r} \\ &= \frac{e^2}{mc^2} \sum_{\mathbf{p}} \left\{ N^+(\mathbf{p}) u^+(\mathbf{p})^* \beta_4^2 (\beta \mathbf{A}_0)^2 \beta_4^2 u^+(\mathbf{p}) + \right. \\ &\quad \left. (N^-(\mathbf{p}) + 1) u^-(\mathbf{p})^* \beta_4^2 (\beta \mathbf{A}_0)^2 \beta_4^2 u^-(\mathbf{p}) \right\} \end{aligned}$$

If we now sum over the directions of polarisation and take the average, we find for a meson with spin one

$$W_{\text{fluct}}^2 = \frac{e^2}{6} \sum_{\mathbf{p}} \left[ 3A_0^2 + \frac{2}{m^2 c^2} \left\{ A_0^2 p^2 - (\mathbf{A}_0 \mathbf{p})^2 \right\} \right]_{AV} \frac{N^+(\mathbf{p}) + N^-(\mathbf{p}) + 1}{E(\mathbf{p})},$$

and for a spinless meson

$$W_{\text{fluct}}^2 = \frac{e^2}{2} (A_0^2)_{AV} \sum_{\mathbf{p}} \frac{N^+(\mathbf{p}) + N^-(\mathbf{p}) + 1}{E(\mathbf{p})}$$

Thus for a positive meson at rest ( $\mathbf{p} = 0$ ), we have in both the cases

$$W_{\text{fluct}}^2 = W_{\text{fluct}}^2 (\text{vac} + 1) - W_{\text{fluct}}^2 (\text{vac}) = \frac{e^2}{2mc^2} (A_0^2)_{AV} \quad \dots (51)$$

We write  $\mathbf{i}_1 = \mathbf{i}_1^0 + \mathbf{i}_1'$ , where  $\mathbf{i}_1^0$  is calculated for free meson and  $\mathbf{i}_1'$  is the correction obtained by first order perturbation theory. Now if

$$\psi_0 = \sum_{\mathbf{p}} \{ a(\mathbf{p}) \phi^+(\mathbf{p}) + b^*(\mathbf{p}) \phi^-(\mathbf{p}) \} \quad \dots (52)$$

is the wave function unperturbed by the field and  $\psi_1$  is the correction in the first order perturbation theory.

$$\psi_1 = \sum_{\mathbf{p}} \{ a(\mathbf{p}) \phi^+(\mathbf{p})' + b^*(\mathbf{p}) \phi^-(\mathbf{p})' \}, \quad \dots (53)$$

then

$$\begin{aligned} \mathbf{i}_1^0 &= \frac{ie\hbar}{mc} \frac{\partial \psi_0^*}{\partial x_k} \beta_4^2 \beta_k \beta_4^2 \psi_0 + \text{conj.}, \\ \mathbf{i}_1' &= \frac{ie\hbar}{mc} \left\{ \frac{\partial \psi_0^*}{\partial x_k} \beta_4^2 \beta_k \beta_4^2 \psi_1 - \psi_0^* \beta_4^2 \beta_k \beta_4^2 \frac{\partial \psi_1}{\partial x_k} \right\} + \text{conj.} \quad \dots (54) \end{aligned}$$

to a first approximation. It is evident that the term  $(\mathbf{i}_1^0 \mathbf{A}_0)$  has no diagonal elements because there is no phase relation between  $\mathbf{i}_1^0$  and  $\mathbf{A}_0$ . Again if we substitute (52) and (53) in (54), and retain only the diagonal elements we get

$$i_1' = \frac{ie\hbar}{mc} \sum_{\mathbf{p}} \left[ N^+(\mathbf{p}) \left\{ \frac{\partial \phi^+(\mathbf{p})}{\partial x_k} \beta_4^2 \beta_k \beta_4^2 \phi^+(\mathbf{p})' - \phi^+(\mathbf{p})^* \beta_4^2 \beta_k \beta_4^2 \frac{\partial \phi^+(\mathbf{p})'}{\partial x_k} \right\} \right. \\ \left. + (N^-(\mathbf{p}) + 1) \left\{ \frac{\partial \phi^-(\mathbf{p})}{\partial x_k} \beta_4^2 \beta_k \beta_4^2 \phi^-(\mathbf{p})' - \phi^-(\mathbf{p})^* \beta_4^2 \beta_k \beta_4^2 \frac{\partial \phi^-(\mathbf{p})'}{\partial x_k} \right\} \right] + \text{conj}$$

Hence for a single positive meson at rest ( $\mathbf{p} = 0$ )

$$i_1' = i_1'(\text{vac} + 1) - i_1'(\text{vac}) = -\frac{ie\hbar}{mc} \phi^+(0)^* \beta_4^2 \beta_k \beta_4^2 \frac{\partial \phi^+(0)'}{\partial x_k} + \text{conj} \quad (55)$$

$\phi^+(\mathbf{p})'$  can be calculated by the usual first order perturbation theory expanding the vector potential  $\mathbf{A}_0$  in a Fourier series

$$\mathbf{A}_0 = \sum_{\mathbf{k}} \mathbf{e}_{\mathbf{k}} \left[ A_{\mathbf{k}}^+ \exp \frac{i}{\hbar} \{ (\mathbf{k}\mathbf{r}) + c|\mathbf{k}|t \} + A_{\mathbf{k}}^- \exp -\frac{i}{\hbar} \{ (\mathbf{k}\mathbf{r}) + c|\mathbf{k}|t \} \right]$$

If we take solutions for free meson in the form (7) and (8), we obtain for  $\phi^+(\mathbf{p})'$

$$\phi^+(\mathbf{p})' = e \sum_{\mathbf{p}'} \left[ u^+(\mathbf{p}')^* \beta_4^2 \left\{ 1 - \frac{i}{mc} (\mathbf{p}'\mathbf{p}) \right\} (\beta \mathbf{e}_{\mathbf{k}}) u^+(\mathbf{p}) \right. \\ \times \left\{ A_{\mathbf{k}}^+ \frac{\exp \frac{i}{\hbar} \{ E(\mathbf{p}') - E(\mathbf{p}) + c|\mathbf{k}| \} t}{E(\mathbf{p}') - E(\mathbf{p}) + c|\mathbf{k}|} + A_{\mathbf{k}}^- \frac{\exp \frac{i}{\hbar} \{ E(\mathbf{p}') - E(\mathbf{p}) - c|\mathbf{k}| \} t}{E(\mathbf{p}') - E(\mathbf{p}) - c|\mathbf{k}|} \right\} \phi^+(\mathbf{p}') \\ + u^-(\mathbf{p}')^* \beta_4^2 \left\{ 1 - \frac{i}{mc} (\mathbf{p}'\mathbf{p}) \right\} (\beta \mathbf{e}_{\mathbf{k}}) u^-(\mathbf{p}) \left\{ A_{\mathbf{k}}^+ \frac{\exp -\frac{i}{\hbar} \{ E(\mathbf{p}') + E(\mathbf{p}) - c|\mathbf{k}| \} t}{E(\mathbf{p}') + E(\mathbf{p}) - c|\mathbf{k}|} \right. \\ \left. + A_{\mathbf{k}}^- \frac{\exp -\frac{i}{\hbar} \{ E(\mathbf{p}') + E(\mathbf{p}) + c|\mathbf{k}| \} t}{E(\mathbf{p}') + E(\mathbf{p}) + c|\mathbf{k}|} \right\} \phi^-(\mathbf{p}') \right] \quad (56)$$

where  $\mathbf{k} = \pm(\mathbf{p}' - \mathbf{p})$ , + sign for the terms with  $A_{\mathbf{k}}^+$  and - sign for the terms with  $A_{\mathbf{k}}^-$ . Replacing  $\phi^+(0)'$  in (55) by the corresponding expression as obtained from (56) we sum over the polarisations in the intermediate states and average over those of the state  $\mathbf{p} = 0$ , and obtain after some calculations  $i_1' = 0$  both for spins one and zero. Hence  $W_{\text{fluct}}^1$  contributes nothing to the self-energy.

Finally from (50) and (51) we get for a meson at rest with spin one or zero

$$W_{\text{fluct}} = \frac{e^2}{2mc^2} (A_0^2)_{A'}$$

which is the same as the corresponding expression for the Dirac electron as given by Weisskopf and so we can take his result

$$W_{\text{fluct}} = \frac{e^2 \kappa}{\pi} \lim_{P \rightarrow \infty} \left( \frac{P}{mc} \right)^2 \quad (57)$$

Thus we have from (26), for spinless meson [Eqns (44), (47) and (57)]

$$W_{\text{tr}} = \frac{e^2 \kappa}{\pi} \lim_{P \rightarrow \infty} \left( \frac{P}{mc} \right)^2, \quad (58)$$

$U_{\text{el}}$  and  $U_{\text{mag}}$  being zero as the particle has no spin, and for meson with spin one [Eqns (45), (48) and (57) which agree with the corresponding results as given by Richtmyer]

$$W_{\text{tr}} = \frac{e^2 \kappa}{6\pi} \lim_{P \rightarrow \infty} \left[ 6 \left( \frac{P}{mc} \right)^2 - \frac{P \sqrt{P^2 + m^2 c^2}}{m^2 c^2} + \log \frac{P + \sqrt{P^2 + m^2 c^2}}{mc} \right] \quad (59)$$

$$= \frac{e^2 \kappa}{6\pi} \lim_{P \rightarrow \infty} \left[ 5 \left( \frac{P}{mc} \right)^2 + \log \left( \frac{P}{mc} \right) \right] + \text{finite terms} \quad (60)$$

where it should be noticed that portions of  $U_{\text{el}}$  and  $U_{\text{mag}}$ , which diverge as  $P^4$ , cancel one another. Hence in both the cases the transverse part as well as the static part of the self-energy diverge quadratically, so also the total self-energy. It will be shown in the next section that these transverse self-energies can be obtained directly by a second order perturbation calculation.

## 6 DIRECT CALCULATIONS OF TRANSVERSE SELF-ENERGY BY SECOND ORDER PERTURBATION

The interaction terms in the Hamiltonian due to the transverse electromagnetic field are given by (15) and (16) which can be written in the forms

$$H^1 = - \frac{e}{mc} \int \psi^* \beta_4^2 \{ (\mathbf{p}\beta)(\mathbf{A}\beta) + (\mathbf{A}\beta)(\mathbf{p}\beta) \} \beta_4^2 \psi d\mathbf{r} \quad (61)$$

which is linear in  $\mathbf{A}$ , and where the first  $\mathbf{p}$  operates backward on  $\psi^*$  and the second  $\mathbf{p}$  operates forward on  $\psi$ , and

$$H^2 = \frac{e^2}{mc^2} \int \psi^* \beta_4^2 (\mathbf{A}\beta)^2 \beta_4^2 \psi d\mathbf{r} \quad (62)$$

which is quadratic in  $\mathbf{A}$ . We expand  $\mathbf{A}$  as a Fourier series

$$\mathbf{A} = \sum_k \sqrt{\frac{2\pi c \hbar^2}{k}} \mathbf{e}_k \left\{ C_k e^{\frac{i}{\hbar}(\mathbf{k}\mathbf{r})} + C_k^* e^{-\frac{i}{\hbar}(\mathbf{k}\mathbf{r})} \right\}, \quad \dots \quad (63)$$

where  $\mathbf{e}_k$  is a real unit vector in the direction of polarisation of the Fourier component  $\mathbf{k}$  ( $k = \frac{\hbar \omega}{c}$ ), and  $\psi$  as

$$\psi = \sum_p \{ a(\mathbf{p}, t) u^+(\mathbf{p}) + b^*(\mathbf{p}, t) u^-(\mathbf{p}) \} e^{i\hbar(\mathbf{p} \cdot \mathbf{x})} \quad \dots (64)$$

Now inserting these values of  $\psi$  and  $\mathbf{A}$  in (61) and (62), we obtain

$$\begin{aligned} H^1 = & -\frac{e\hbar}{mc} \sum_{p'} \sum_p \sum_k \sqrt{\frac{2\pi c}{k}} \{ a^*(\mathbf{p}') u^+(\mathbf{p}')^* + b(\mathbf{p}') u^-(\mathbf{p}')^* \} \\ & \times \beta_4^2 \{ (\mathbf{p}'\beta)(\mathbf{e}_k\beta) + (\mathbf{e}_k\beta)(\mathbf{p}\beta) \} \beta_4^2 \{ C_k \delta(\mathbf{p} - \mathbf{p}' + \mathbf{k}) + C_k^* \delta(\mathbf{p} - \mathbf{p}' - \mathbf{k}) \} \\ & \times \{ a(\mathbf{p}) u^+(\mathbf{p}) + b^*(\mathbf{p}) u^-(\mathbf{p}) \}, \end{aligned} \quad (65)$$

and

$$\begin{aligned} H^2 = & \frac{2\pi e^2 \hbar^2}{mc} \sum_{p'} \sum_p \sum_k \sum_{k'} \frac{1}{\sqrt{k k'}} \{ a^*(\mathbf{p}') u^+(\mathbf{p}')^* + b(\mathbf{p}') u^-(\mathbf{p}')^* \} \\ & \times \beta_4^2 (\mathbf{e}_k\beta) (\mathbf{e}_{k'}\beta) \beta_4^2 \{ C_k C_{k'} \delta(\mathbf{p} - \mathbf{p}' + \mathbf{k} + \mathbf{k}') + C_k C_{k'}^* \delta(\mathbf{p} - \mathbf{p}' + \mathbf{k} - \mathbf{k}') \\ & + C_k^* C_{k'} \delta(\mathbf{p} - \mathbf{p}' - \mathbf{k} + \mathbf{k}') + C_k^* C_{k'}^* \delta(\mathbf{p} - \mathbf{p}' - \mathbf{k} - \mathbf{k}') \} \{ a(\mathbf{p}) u^+(\mathbf{p}) + b^*(\mathbf{p}) u^-(\mathbf{p}) \} \end{aligned} \quad (66)$$

It is well known that the operators  $a^*$  and  $b^*$  respectively increase the number of positive and negative mesons by one, whereas  $a$ ,  $b$  without asterisk decrease the corresponding number of mesons by one. The operator  $C^*$  increases the number of photons by one, whereas  $C$  decreases it by one. The interaction  $H^1$  gives rise to various transitions involving one light quantum, but  $H^2$  gives rise to transitions in which two light quanta are concerned.

The second approximation to the interaction energy is given by

$$W = W_1 + W_2 = \sum_n \frac{H_{n,1}^1 H_{1,n}^1}{E_n - E_1} + H_{nn}^2 \quad (67)$$

where the summation is to be taken over all intermediate states. We consider the case of free positive meson at rest ( $\mathbf{p} = 0$ ). We assume that in the state  $n$  for which we compute the average energy no light quanta are present. We have the following set of transitions to consider from (65) and (66)

1. The meson  $u^+(0)$  is absorbed, and a light quantum  $\mathbf{k}$  and the meson  $u^+(-\mathbf{k})$  are emitted.

$$H_{1n}^1 = \frac{e\hbar}{mc} \sqrt{\frac{2\pi c}{k}} u^+(-\mathbf{k})^* \beta_4^2(\mathbf{k}\beta) (\mathbf{e}\beta) \beta_4^2 u^+(0). \quad (68)$$

The light quantum  $\mathbf{k}$  and the meson  $u^+(-\mathbf{k})$  are then absorbed and the meson  $u^+(0)$  is emitted

$$H_{nI}^1 = \frac{e\hbar}{mc} \sqrt{\frac{2\pi c}{k}} u^+(0)^* \beta_4^2(\mathbf{e}\beta)(\mathbf{k}\beta) \beta_4^2 u^+(-\mathbf{k}) \quad (69)$$

2 The light quantum  $-\mathbf{k}$  is emitted and a pair of mesons  $u^+(0)$  and  $u^-(-\mathbf{k})$  are created

$$H_{II n}^1 = \frac{e\hbar}{mc} \sqrt{\frac{2\pi c}{k}} u^+(0)^* \beta_4^2(\mathbf{e}\beta)(\mathbf{k}\beta) \beta_4^2 u^-(-\mathbf{k}) \quad (70)$$

The light quantum  $-\mathbf{k}$  is then absorbed and a pair of mesons  $u^+(0)$  and  $u^-(-\mathbf{k})$  are annihilated

$$H_{nII}^1 = \frac{e\hbar}{mc} \sqrt{\frac{2\pi c}{k}} u^-(-\mathbf{k})^* \beta_4^2(\mathbf{k}\beta)(\mathbf{e}\beta) \beta_4^2 u^+(0) \quad \dots \quad (71)$$

3 The meson  $u^+(0)$  and the light quantum  $\mathbf{k}$  are emitted, and simultaneously the meson  $u^+(-\mathbf{k})$  and the light quantum  $\mathbf{k}$  are absorbed

$$H_{nn}^2 = \frac{4\pi e^2 \hbar^2}{mc} \frac{1}{k} u^+(0)^* \beta_4^2(\mathbf{e}\beta)^2 \beta_4^2 u^+(-\mathbf{k}). \quad \dots \quad (72)$$

The energy differences  $E_n - E_i$  are given by

$$E_n - E_I = E(0) - ck - E(-\mathbf{k}) = mc^2 - ck - E(-\mathbf{k}),$$

$$E_n - E_{II} = E(0) - \{2E(0) + ck + E(-\mathbf{k})\} = -mc^2 - ck - E(-\mathbf{k})$$

From equations (68-71), we then get

$$W_1 = \frac{2\pi e^2 \hbar^2}{m^2 c} \frac{1}{k} \left[ \frac{\{u^+(0)^* \beta_4^2(\mathbf{e}\beta)(\mathbf{k}\beta) \beta_4^2 u^+(-\mathbf{k})\} \{u^+(-\mathbf{k})^* \beta_4^2(\mathbf{k}\beta)(\mathbf{e}\beta) \beta_4^2 u^+(0)\}}{mc^2 - ck - E(-\mathbf{k})} \right. \\ \left. - \frac{\{u^+(0)^* \beta_4^2(\mathbf{e}\beta)(\mathbf{k}\beta) \beta_4^2 u^-(-\mathbf{k})\} \{u^-(-\mathbf{k})^* \beta_4^2(\mathbf{k}\beta)(\mathbf{e}\beta) \beta_4^2 u^+(0)\}}{mc^2 + ck + E(-\mathbf{k})} \right], \quad (73)$$

and from (72)

$$W_2 = \frac{4\pi e^2 \hbar^2}{mc} \frac{1}{k} u^+(0)^* \beta_4^2(\mathbf{e}\beta)^2 \beta_4^2 u^+(-\mathbf{k}). \quad \dots \quad (74)$$

We now sum over the polarisations of meson in the intermediate state  $-\mathbf{k}$  and average over that of the initial state; then summing over both directions of polarisation of photon, we obtain from (73) for a spinless meson

$$W_1 = 0,$$

and for a meson with spin one

$$W_1 = -\frac{2\pi e^2 \hbar^2}{3m} \cdot \frac{1}{E(-\mathbf{k})}$$

Again for  $W_2$  given by (74) if we average over the polarisations in the state  $p = 0$ , and sum over that of the photon, we get in both the cases

$$W_2 = \frac{4\pi e^2 \hbar^2}{mc} \frac{1}{k}.$$

We shall now have to sum over all light quanta and this summation can be replaced by an integration. Hence for a spinless meson

$$W = \frac{4\pi e^2 \hbar^2}{mc} \frac{1}{(2\pi \hbar)^3} \int \frac{d\mathbf{k}}{k} = \frac{e^2 \kappa}{\pi} \lim_{P \rightarrow \infty} \left( \frac{P}{mc} \right)^2, \quad (75)$$

and for a meson with spin one

$$\begin{aligned} W &= \frac{4\pi e^2 \hbar^2}{mc} \frac{1}{(2\pi \hbar)^3} \int \frac{d\mathbf{k}}{k} - \frac{2\pi e^2 \hbar^2}{3mc} \frac{1}{(2\pi \hbar)^3} \int \frac{d\mathbf{k}}{\sqrt{k^2 + m^2 c^2}} \\ &= \frac{e^2 \kappa}{6\pi} \lim_{P \rightarrow \infty} \left[ 6 \left( \frac{P}{mc} \right)^2 - \frac{P \sqrt{P^2 + m^2 c^2}}{m^2 c^2} + \log \frac{P + \sqrt{P^2 + m^2 c^2}}{mc} \right]. \quad (76) \end{aligned}$$

Thus (75) is in agreement with (58) and (76) with (59). It should be noticed that for a meson at rest the interacting term  $H^2$  contributes only to that part of the self-energy which is produced by the zero-point fluctuations of the radiation field, while  $H^1$  is responsible for the part which depends on the spin.

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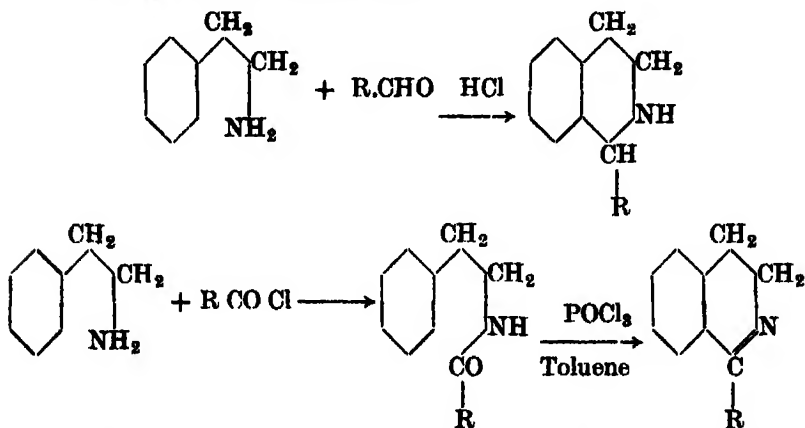
## STUDIES IN THE ISOQUINOLINE SERIES

### PART XI THE INFLUENCE OF ALKYL- AND ARYL-SUBSTITUENTS IN THE SIDE CHAINS OF ACYL- $\beta$ , PHENYL ETHYL AMIDES ON THE CLOSURE OF THE ISOQUINOLINE RING

By B B DEY and V S RAMANATHAN

(Received November 6, 1942)

Two of the best known reactions by which isoquinoline derivatives may be prepared consist in the condensation of bases of the  $\beta$ -phenyl ethyl amine type with either alphatic aldehydes in the presence of HCl or with esters or acid chlorides or acid anhydrides followed by treatment with such powerful dehydrating agents as phosphoryl chloride or phosphorus pentoxide in boiling toluene, xylene or tetraline, thus —

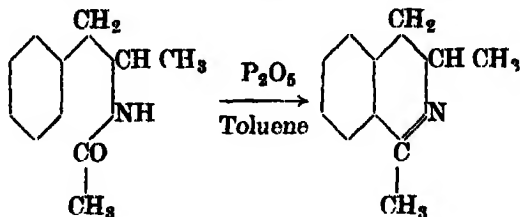


In the former reaction studied by Pictet (1911), Decker and others (1913), tetrahydro-isoquinoline derivatives are obtained whilst the latter studied by Bischler and Napieralsky (1893) and known by their name, and modified later by Pictet (1909; 1910) and Decker (1909) leads to the formation of the 3,4, dihydro-isoquinolines which may either be oxidised to the isoquinolines or reduced to the tetrahydro-compounds. The syntheses of the natural alkaloids containing the isoquinoline ring have generally been carried out by the Bischler-Napieralsky method and hence its importance.

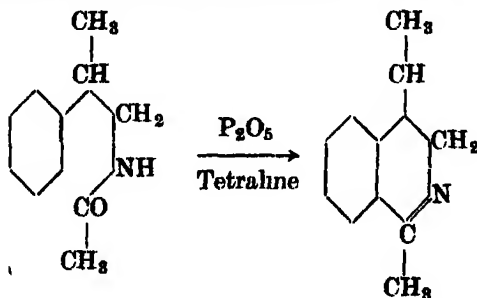
Although this method has been employed extensively in the field of isoquinoline syntheses, a perusal of literature does not reveal any systematic attempts having been made to study the influence of different groups, such as methyl, phenyl or benzyl in the side chain, on the ring closure of the acyl derivatives of  $\alpha$ - and  $\beta$ -substituted  $\beta$ -phenyl ethyl amines. As far as can be

ascertained from literature, syntheses of the following isoquinolines with alkyl or aryl substituents in 3 and 4 positions in the pyridine nucleus, have hitherto been carried out.—

(a) 1,3, dimethyl-3,4, dihydro-isoquinoline. [Hey, 1930]

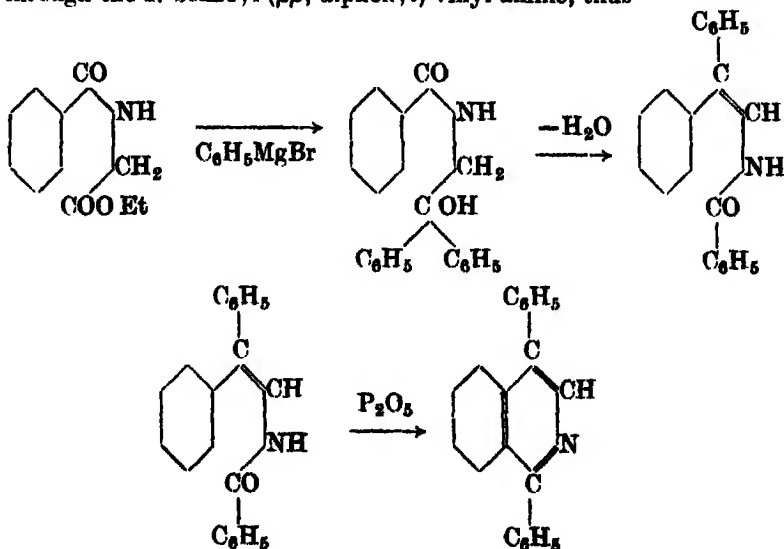


(b) 1,4, dimethyl-3,4, dihydro-isoquinoline [Spath, 1930]



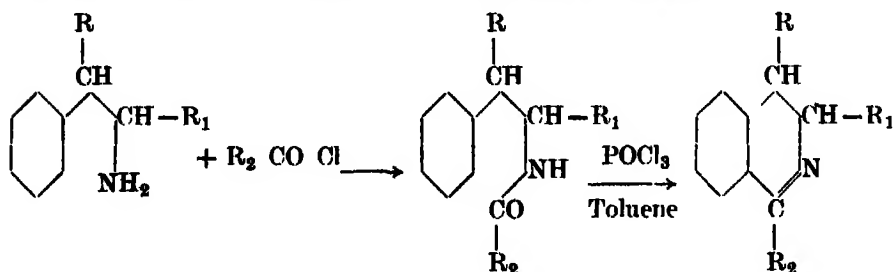
(c) 1, methyl-4, phenyl-1,4, diphenyl- and 1, methyl-3,4, diphenyl-isoquinolines [Krabbe, 1936, Krabbe *et al*, 1938]

N-benzoyl-amino-methyl diphenyl carbinol, obtained from hippuric ester and phenyl magnesium bromide, was converted into 1,4, diphenyl isoquinoline through the N-benzoyl ( $\beta\beta$ , diphenyl)-vinyl amine, thus —



The object of the present investigation has been to study the influence of both alkyl and aryl groups in the side chains of  $\beta$ , phenyl ethyl amines, on the facility or otherwise with which the acyl derivatives of the amines could be cyclised to the isoquinolines

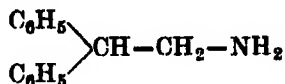
The study has necessarily entailed the preparation, in the first stage, of a number of  $\alpha$ , and  $\beta$ , substituted  $\beta$ -phenyl ethyl amines, the substituents being methyl, phenyl and benzyl groups, of their acet-, benz-, and phenyl acetamides in the second stage, and the cyclisation of these amides finally to the corresponding 3,4 dihydro isoquinolines by one standard method, viz that of warming the amides in toluene solution with phosphoryl chloride. The reactions involved are explained in the schemes given below —



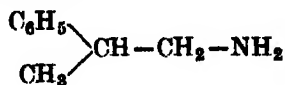
where  $\text{R}$ ,  $\text{R}_1$ , and  $\text{R}_2 = \text{H}$ ,  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ , or  $\text{CH}_2 - \text{C}_6\text{H}_5$

The following substituted  $\beta$ , phenyl ethyl amines have been employed in the present investigations —

A  $\beta\beta$ , diphenyl-ethyl amine.



B  $\beta$ , methyl- $\beta$ , phenyl ethyl amine



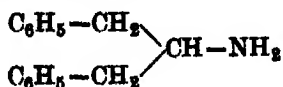
C  $\alpha$ , methyl- $\beta$ , phenyl ethyl amine

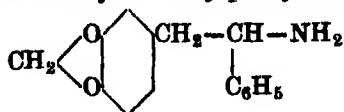


D  $\alpha$ , phenyl- $\beta$ , phenyl ethyl amine

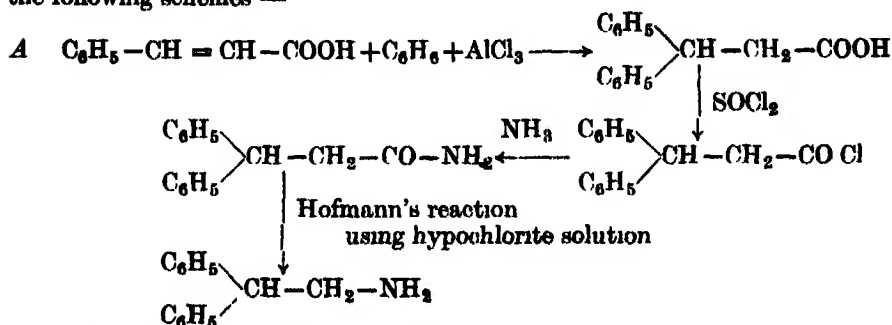


E  $\alpha$ , benzyl- $\beta$ , phenyl ethyl amine

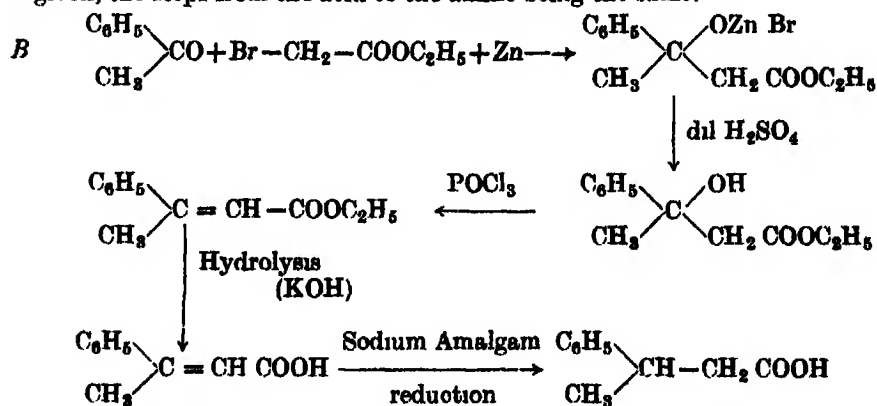


F  $\alpha$ , phenyl- $\beta$ , 3 4 methylenedioxy-phenyl-ethyl amine

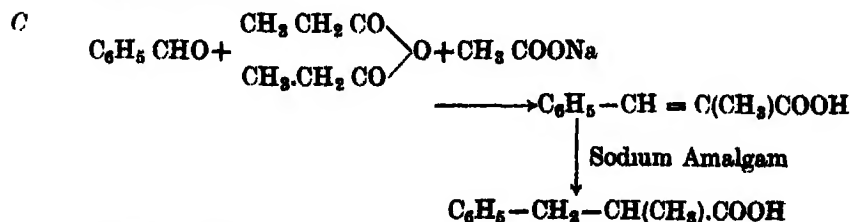
All the amines with the exception of E ( $\alpha$ , benzyl- $\beta$ , phenyl ethyl amine), were prepared by the well-known method of Hofmann using the corresponding acids as the starting material. The steps employed in the preparation of the individual amines (A, B, C, D, E, and F) mentioned above are explained in the following schemes—

[Vorlander *et al*, 1923]

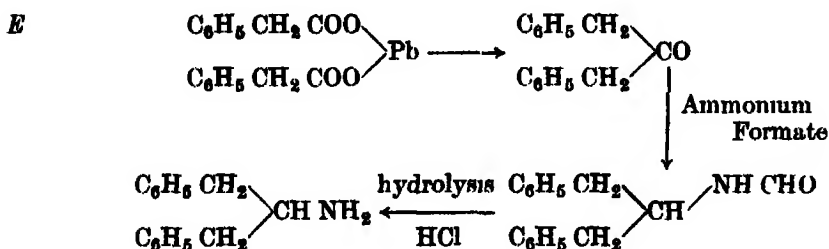
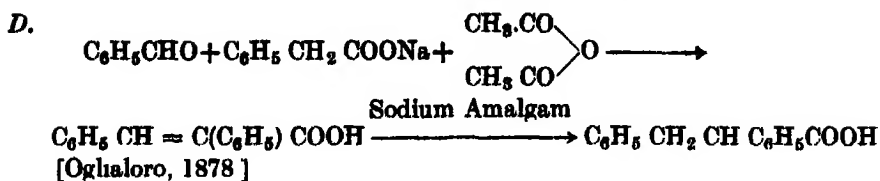
In the cases of the other amines, the preparation up to the acid stage only is given, the steps from the acid to the amine being the same.



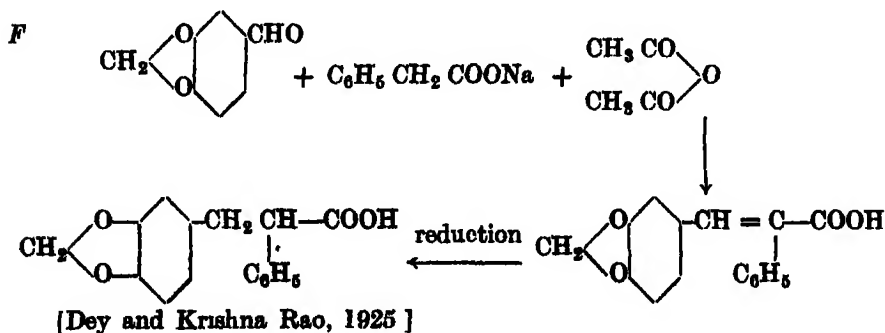
[Lindenbaum, 1917]



[Edeleano, 1887]



Dibenzyl ketone has been prepared by Apitzsch (1904) and Young (1891) by the dry distillation of the calcium salt of phenyl acetic acid Kenner and Morton (1939) obtained the same ketone by dry distillation of the lead salt. The distillation of the lead salt was preferred as its decomposition temperature was much lower than that of the calcium salt. The ketone was converted to the amine by the method of Leuckart modified by Ingersoll *et al*, (1936)

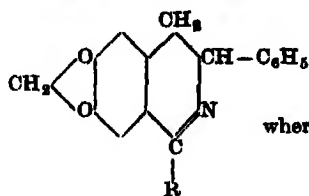


The results obtained are given in the accompanying table. The yields of the isoquinolines obtained by cyclising under identical conditions the acyl derivatives of the unsubstituted  $\beta$ , phenyl ethyl amine have been adopted as the standards of reference for the comparison and correlation of the results obtained with all the other substituted amines. The experimental conditions were kept rigidly constant and the element of error through accidents was carefully eliminated by repeating the cyclisations at least twice in each case until the results were strictly concordant.

The yields of the isoquinolines obtained by cyclising the acyl derivatives of  $\alpha$ , methyl- $\beta$ , phenyl ethyl amine are found to be comparatively higher than those of  $\beta$ , methyl- $\beta$ , phenyl ethyl amine thus showing that the methyl group in  $\alpha$ , position facilitates cyclisation to a greater extent than that in the  $\beta$ ,

position A glance at the table would show that the yield of 1,3, dimethyl-3,4-dihydro-isoquinoline (48 per cent) and 1, benzyl-3, methyl-3,4, dihydro-isoquinoline (45 per cent) are higher than those of 1,4, dimethyl-dihydro-isoquinoline (31 per cent) and 1, benzyl-4, methyl-3,4, dihydro-isoquinoline (38 per cent). The introduction of the phenyl group in 1, position is however found to reduce the yield of 3, methyl-dihydro-isoquinoline and to increase the yield of the 4, methyl-dihydro-isoquinoline. The inference is obvious that the influence of the group in position 1, i.e. the acyl group in the amide cannot be ignored or neglected. In one case the phenyl group in 1, position seems to be favourable for cyclisation whereas in the other it appears to retard. The phenyl group in  $\beta$ , position in the acyl derivatives of  $\beta$ ,  $\beta$ , diphenyl ethyl amine has practically little or no influence on cyclisation. Here again, 1,4 diphenyl-3,4, dihydro-isoquinoline stands as an exception. A much higher yield of the isoquinoline was obtained showing that the phenyl group in 1, position influences the reaction facilitating ring closure. A perusal of the table shows that none of the acyl derivatives of  $\alpha$ ,  $\beta$ , diphenyl ethyl amine could be cyclised indicating the probable retarding effect of the phenyl group.

No	Substituents in different positions in 3,4, dihydro isoquinolines			Yield in per cent of that required by theory
	Position 1	Position 3	Position 4	
1	Methyl	Nil	Nil	22 (standard)
	Phenyl	"	"	26 "
	Benzyl	"	"	9 "
2	Methyl	Methyl	"	48 "
	Phenyl	"	"	35 "
	Benzyl	"	"	45 "
3	Methyl	Nil	Methyl	31
	Phenyl	"	"	45
	Benzyl	"	"	38
4	Methyl	Phenyl	Nil	Nil
	Phenyl	"	"	"
	Benzyl	"	"	"
5	Methyl	"	Phenyl	28
	Phenyl	"	"	53
	Benzyl	"	"	9
6	Methyl	*6-7 (Methylene dioxy) phenyl	Nil	60
	Phenyl	"	"	25
	Benzyl	"	"	45
7	Methyl	Benzyl	"	38
	Phenyl	"	"	11
	Benzyl	"	"	22

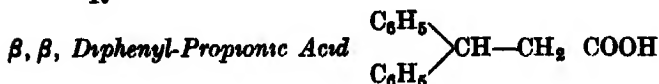
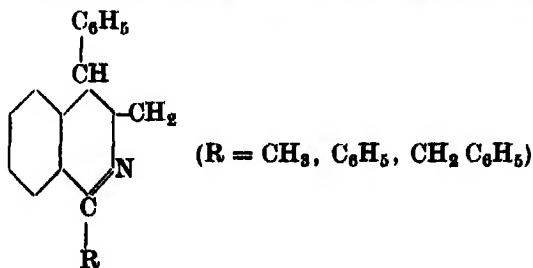


where R =  $-\text{CH}_2-\text{C}_6\text{H}_5$  or  $-\text{CH}_2-\text{C}_6\text{H}_5$

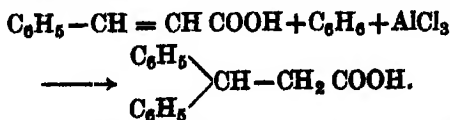
situated in the  $\alpha$ , position It is interesting to note that the retarding effect of the  $\alpha$ , phenyl group would be overcome by using the corresponding  $\alpha$ , phenyl substituted homopiperonyl amine, the methylene dioxy group in the latter activating the para hydrogen atom sufficiently strongly to cause cyclisation to take place in spite of the presence of the  $\alpha$ , phenyl group Here again, when one compares the yields of the 3, phenyl isoquinolines obtained from the acet- $\alpha$ , phenyl homopiperonyl amide and benz- $\alpha$ , phenyl homopiperonyl amide, the same interesting observation is made that the methyl group in 1, position is more helpful than the phenyl group in the same position This illustrates further the rule arrived at above that apart from the influence of the various groups in 3 and 4 positions of the isoquinoline ring, the substituents in position 1 also exert a more or less profound influence on cyclisation The  $\alpha$ , benzyl group in the acyl derivatives of  $\alpha$ , benzyl- $\beta$ , phenyl ethyl amine facilitates cyclisation but the influence of the group varies according to the nature of the acyl derivatives cyclised Acet- $\alpha$ , benzyl  $\beta$ , phenyl ethyl amide gave the highest yield of the isoquinoline (38 per cent) and benz  $\alpha$ , benzyl  $\beta$ , phenyl ethyl amide gave the lowest yield (11 per cent) Because of the difficulty of preparing  $\beta$ , benzyl  $\beta$ , phenyl ethyl amine, the influence of the benzyl group in that position could not be examined

## EXPERIMENTAL

## SECTION A

*Syntheses of 4, Phenyl-3 4, Dihydro-Isoquinolines*

This was prepared by the action of benzene and aluminium chloride on dry cinnamic acid (Vorlander *et al*, 1923) according to the following equation —



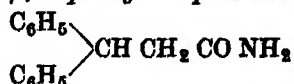
Cinnamic acid (15 g.) was dissolved in dry benzene (190 c.c.) in a 500 c.c. round bottom flask, cooled in ice and anhydrous aluminium chloride (25 g.) added gradually The crystals of cinnamic acid which separated at first

during cooling gradually went into solution. The flask was fitted with a condenser and a  $\text{CaCl}_2$ -tube and allowed to stand for forty-eight hours. The flask was then disconnected, cooled in ice and ice water poured in little by little with vigorous shaking to decompose the aluminium chloride. Concentrated  $\text{HCl}$  was finally added till the solution became clear. The contents of the flask were distilled in steam to remove the benzene and the separating solid filtered hot and washed with hot water several times to remove the unreacted cinnamic acid. The solid diphenyl propionic acid remaining on the filter paper was powdered in a mortar and boiled up twice with about 30 c.c. of water and filtered hot each time by decantation.

The crude diphenyl propionic acid, practically free from cinnamic acid, melted at  $148^\circ$ – $149^\circ$  and weighed 12.5 g. The hot aqueous filtrate deposited on cooling 5.6 g. of nearly pure cinnamic acid (M.P.  $130^\circ$ ).

The diphenyl propionic acid crystallised from ligroin in fine white needles melting at  $152^\circ$ . It is quite insoluble in cold water, slightly in boiling water, sparingly in ligroin and easily in benzene, alcohol and glacial acetic acid.

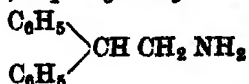
*$\beta\beta$ , Diphenyl-Propionamide*



The dried acid (5 g.) and thionyl chloride (7 c.c.) were mixed in a 100 c.c. round bottomed flask which was then fitted with a condenser carrying a  $\text{CaCl}_2$ -tube and allowed to stand in the cold for 10 minutes. It was then warmed to  $80^\circ$  on a water bath until no more  $\text{HCl}$  fumes could be seen and the excess of thionyl chloride removed under reduced pressure. The residue of acid chloride was dissolved in 30 c.c. of dry benzene, cooled in ice and a stream of ammonia from the cylinder dried by a quicklime tower passed in till there was a strong smell of the gas. The separated solid was filtered after an hour and washed with water to remove the ammonium chloride. The crude amide weighed 4.2 g.

It is sparingly soluble in cold benzene but dissolves readily in the hot solvent from which it crystallises in needles. 3.8 g. of the pure amide, M.P.  $125^\circ$ , were obtained.

*$\beta\beta$ , Diphenyl-Ethyl-Amine*

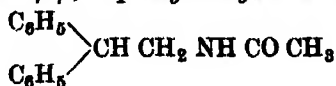


Levy and Galis (1928) and Freund and Immerwahr (1890) have prepared the amine by the reduction of diphenyl-acetaldoxime and diphenyl-acetonitrile. In the present investigation the method of conversion of the amide to the amine by Hofmann's method has been employed.

60 c.c. of a 10 per cent solution of sodium hydroxide was cooled well in ice and chlorine generated from 1.7 g. of potassium permanganate passed into it.

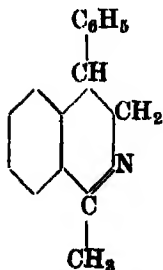
The amide (5 g) was finely powdered and put into the hypochlorite solution which was shaken vigorously and warmed on a water bath at 50°. When the amide had gone completely into solution the temperature was raised to 70° and maintained there for two hours, cooled, 15 g of solid caustic potash added and the mixture again heated to 80°. It was finally cooled, extracted twice with 30 c c of benzene and the benzene layer was shaken six times with dilute HCl. The acid layer was separated basified with sodium hydroxide, and extracted thrice with benzene, the benzene extract was dried over potassium carbonate and the benzene removed by distillation. The diphenyl ethyl amine was obtained as a highly basic oil weighing 2.1 g. It formed a hydrochloride M P 255–256°, and a picrate, M P 212°.

*Acet-β β, Diphenyl-Ethyl Amide*



The amine was rubbed with acetic anhydride, till a faint smell of acetic anhydride persisted. The solid formed was treated with water and warmed to decompose the excess acetic anhydride and filtered and washed with water. It crystallised from dilute alcohol in needles, M P 80°. The yield is quantitative.

1. *Methyl-4, Phenyl-3, 4, Dihydro-Isoquinoline*



The dry acetyl derivative (3 g) was taken in a 60 c c flask. Toluene dried over sodium (10 c c.) and phosphoryl chloride (7 c c) were successively added and the flask fitted with an air condenser carrying a CaCl<sub>2</sub>-tube and heated on an oil bath at 110°–120° for two hours. The contents were slowly poured on to crushed ice (50 g) with vigorous stirring and after standing for an hour, the toluene layer was carefully removed in a separating funnel and the aqueous layer extracted twice with 10 c c of benzene to remove non-basic impurities. A small amount of a sticky resinous mass was left behind from which the clear aqueous layer was decanted off, strongly basified with alkali and extracted thrice with ether (50 c c), the ether layer dried over potassium carbonate and the ether distilled off.

An oil was obtained which weighed 0.8 g. Yield, 30 per cent of the theory.

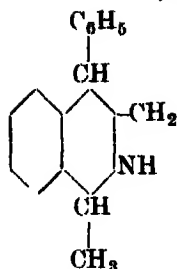
The picrate prepared by the usual method crystallised from alcohol in thick needles. M.P. 169°–170°.

0.1232 g of the picrate gave 1.344 c c of Nitrogen at 31° and 765 mm.

Found N = 12.34 per cent

$\left. \begin{array}{l} \text{C}_{22}\text{H}_{18}\text{O}_7\text{N}_4 \\ (\text{C}_{10}\text{H}_{16}\text{N} \cdot \text{C}_6\text{H}_5\text{O}_7\text{N}_3) \end{array} \right\} \text{ requires N} = 12.44 \text{ per cent}$

## 1, Methyl-4, Phenyl-1, 2, 3, 4, Tetra Hydro-Isoquinoline



The dihydro isoquinoline (1 g) was dissolved in 15 c c of 4N sulphuric acid in a small flask, zinc dust (2 g) added and the mixture heated on a water bath for three hours. The solution was filtered hot, the residue was washed well with boiling water and the filtrate basified strongly with caustic soda. Extraction with ether, drying over potassium carbonate and removal of the ether left the tetrahydro-isoquinoline as a nearly colourless oil weighing 0.6 g.

The benzoyl derivative was prepared by shaking with benzoyl chloride and excess of alkali. It crystallised from alcohol in needles, M P 107°.

0.02396 g gave 1.038 c c of Nitrogen at 35° and 756 mm.

Found N = 4.6 per cent

C<sub>23</sub>H<sub>21</sub>ON requires N = 4.3 per cent

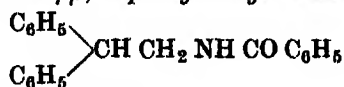
The hydrochloride was prepared by rubbing with concentrated HCl, drying in the desiccator and crystallising from a mixture of alcohol and ether. M P 216°.

0.1648 g of the hydrochloride gave 0.0919 g of AgCl.

Found Cl = 13.79 per cent

C<sub>16</sub>H<sub>17</sub>N HCl requires Cl = 13.68 per cent

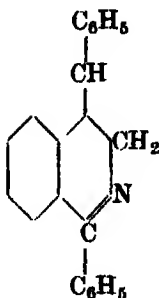
## Benz-ββ, Diphenyl Ethyl Amide



[Cf Lavy and Gaths, 1928]

This was prepared in quantitative yield from the amine and benzoyl chloride by shaking with alkali. It crystallised from alcohol in fine needles. M P 143°.

## 1, 4, Diphenyl-3, 4, Dihydro-Isoquinoline



A mixture of the benzamide (1 g) dry toluene (8 c c) and phosphoryl chloride (3 c c) was heated on an oil bath at 120° for two hours and the product worked in the same way as that mentioned in the case of the 1, methyl-isoquinoline.

The diphenyl isoquinoline was obtained as a pale yellow solid, the yield of the crude product being 0.5 g (53 per cent of theory). It crystallised from methyl alcohol in rhombs. M P 124°.

0.1244 g gave 0.4078 g of carbon dioxide and 0.0676 g of water.

0.1167 g gave 51 c c of Nitrogen at 30° and 757.5 mm.

Found C = 89.41, H = 6.04, N = 4.91 per cent

C<sub>21</sub>H<sub>17</sub>N requires C = 89.04, H = 6.00, N = 4.94 per cent

The *picrate* prepared in the usual way, crystallised from alcohol in thin needles M P 157°

0.1078 g of the *picrate* gave 10.4 c.c. of Nitrogen at 33° and 762 mm

Found N = 10.79 per cent

$C_{27}H_{20}O_7N_4$  requires N = 10.93 per cent

The *hydrochloride* was prepared by dissolving the isoquinoline in dry ether and by passing dry HCl gas. It was crystallised from alcohol-ether mixture M P 205°

0.1280 g gave 0.0582 g of AgCl

Found Cl = 11.26 per cent

$C_{21}H_{18}NCl$  requires Cl = 11.21 per cent

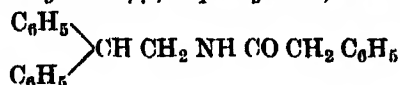
The *methiodide* was prepared by heating the base with excess of methyl iodide in a stoppered bottle at 100° and crystallising the solid product from absolute alcohol. Fine golden yellow needles M P 246°

0.1126 g of the *methiodide* gave 0.0610 g of AgI

Found I = 29.21 per cent

$C_{22}H_{20}NI$  requires I = 29.86 per cent

*Phenyl Acet-ββ, Diphenyl Ethyl Amide*



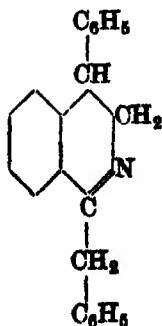
The amine (2.2) was suspended in 10 per cent caustic soda (10 c.c.) cooled in ice and freshly prepared phenyl acetyl chloride (3 g) added drop by drop with good stirring. The amide began to separate almost immediately as a white solid. It was filtered, washed with water and crystallised from hot rectified spirit. Yield, 2.8 g M P 113°

0.1873 g gave 7.8 c.c. of Nitrogen at 33° and 759 mm

Found N = 4.64 per cent

$C_{22}H_{21}ON$  requires N = 4.44 per cent

#### 1, Benzyl-4, Phenyl-3, 4, Dihydro-Isoquinoline



The amide (1 g) was mixed with dry toluene (6 c.c.) and phosphoryl chloride (3 c.c.) in a flask heated to 110° for two hours and the product worked up in the usual way.

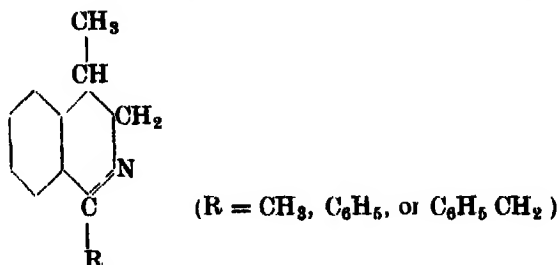
The isoquinoline was obtained as an oil. The yield was poor (0.08 g, i.e. 9 per cent of theory). This was converted into *picrate* which crystallised from alcohol in fine rhombic needles M P 203°

0.0586 g gave 5.7 c.c. of Nitrogen at 32° and 760 mm.

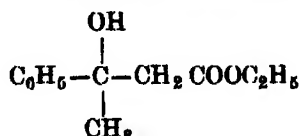
Found N = 10.89 per cent

$C_{28}H_{22}N_4O_7$  } requires N = 10.64 per cent  
 $(C_{22}H_{19}N C_6H_5N_3O_7)$  }

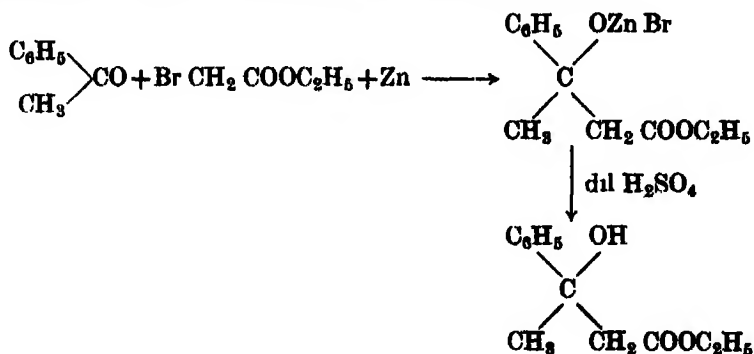
## SECTION B

*Synthesis of 1, substituted 4, -Methyl 3, 4, Dihydro-Isoquinolines*

*ββ, Phenyl Methyl β, Hydroxy-Propionic Ethyl Ester* [Cf Lundenbaum, 1917]



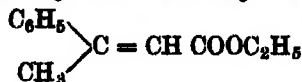
This was prepared from acetophenone and bromacetic ester by Reformatsky's reaction according to the following equation —



Acetophenone (15 g), freshly distilled bromacetic ester (16 g), benzene distilled over sodium (75 c c) and zinc wool (10 g) were taken in a 500 c c round bottomed flask fitted with an efficient condenser. The contents were warmed until reaction had started when the flask was removed from the bath. After the reaction, which was quite vigorous, had subsided, the flask was replaced in the steam bath and boiled for 45 minutes. The brown mass was then treated with dilute sulphuric acid (60 c c.), shaken well to decompose the unreacted zinc and the zinc compound formed, and allowed to stand till the benzene and water layers had completely separated. The benzene layer was carefully removed, repeatedly washed with dilute sulphuric acid (five times), dried over anhydrous calcium chloride and the benzene distilled off.

The ester was then fractionated under reduced pressure, the portion distilling between 132° and 136° under 5 mm being collected separately Yield, 24.6 g

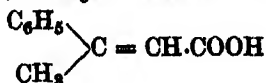
*β Methyl Cinnamic Ethyl Ester*



The hydroxy ester prepared above (24.5 g) was dissolved in perfectly dry benzene (80 c c) phosphoryl chloride (8 c c) added and the mixture boiled in a flask fitted with a condenser on a steam bath for 45 minutes After cooling and adding ice to decompose the excess of phosphoryl chloride the contents were transferred to a 250 c c separating funnel, the benzene layer repeatedly washed with water, dried over calcium chloride and the benzene distilled off

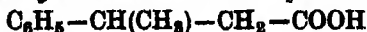
The ester was distilled under reduced pressure, the fraction boiling at 135°–140° under 5 mm being collected It is a colourless liquid with a pleasant smell resembling that of ethyl cinnamate Yield, 20.5 g

*β, Methyl Cinnamic Acid*



The ester (20.5 g) was dissolved in 90 per cent alcohol (50 c c) and a solution of 10 g of caustic potash in 10 c c of water added and boiled on a steam bath for 2½ hours The alcohol was then distilled off (40 c c) and the contents poured into 200 c c of water The solution was extracted twice with benzene to remove unreacted ester, cooled and acidified with concentrated HCl The white solid which separated immediately was filtered and washed thoroughly The uncrystallised acid weighed 15 g and melted at 93°–95° A portion, crystallised from ligroin, melted at 99°

*β, Methyl Hydro cinnamic Acid* [Cf Rupe, 1909]



The crude acid (14.5 g) was taken in 150 c c of water in a strong bolt-head flask, a solution of 2.5 g of caustic soda in 10 c c of water added and warmed to dissolve the acid The solution was stirred mechanically and freshly made 4 per cent sodium amalgam (415 g) added in small quantities at a time The mixture was left overnight, filtered through a Buchner funnel, cooled in ice and acidified with concentrated HCl with stirring The acid which separated as an oil was extracted with benzene, dried over calcium chloride and the benzene distilled off.

The acid distilled as a colourless liquid at 152°–154°, under 5 mm Yield, 13.6 g.

*ββ, Phenyl Methyl Propionamide* [Cf Woodruff and Karl Pierson, 1938 ]  
 $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{CO NH}_2$

The acid (13.6 g) was warmed with thionyl chloride (10 c.c.) at 80° for an hour with the usual precautions and the excess of thionyl chloride removed under reduced pressure. The residual liquid was taken up in 15 c.c. of dry benzene in a separating funnel and added drop by drop to 150 c.c. of liquor ammonia, cooled in ice and stirred mechanically. The amide separated as a snow-white powder which was filtered and the filtrate concentrated when a further small quantity (1.5 g) of the amide was obtained.

Total Yield, 11.5 g

It crystallised from boiling water in fine needles. M.P. 106°

*ββ, Phenyl Methyl Ethyl Amine*  
 $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$

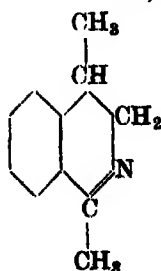
Freund and König (1893) prepared the amine by the reduction of phenyl propionitrile with sodium and alcohol. Woodruff and Karl Pierson (1938) obtained the amine by Hofmann's reaction using sodium hypobromite solution. Here instead of the hypobromite, hypochlorite solution has been employed.

70 c.c. of a 10 per cent solution of sodium hydroxide was cooled in ice and chlorine generated from 2.1 g. of powdered potassium permanganate and concentrated HCl passed in. The powdered amide (5 g) was added to the hypochlorite solution and warmed on a water bath to 45°–50° with frequent shaking. The amide gradually dissolved to a clear solution when the temperature (internal) was raised to 60°–70° and kept at this temperature for two hours. Drops of an oil were found to separate out. Caustic potash (12 g) was then added and the liquid heated to 80° for another ten minutes. On cooling, the amine was extracted with benzene (3 times using 15 c.c. each time) and the benzene layer shaken with dilute hydrochloric acid (6 times using 10 c.c. each time). The acid layer was cooled, basified and extracted completely with benzene and the benzene dried and distilled off. The amine was left behind as a highly basic oil, weighing 3 g.

*Acet-ββ, Phenyl Methyl Ethyl Amide*  $\text{C}_6\text{H}_5\text{—CH}(\text{CH}_3)\text{—CH}_2\text{—NH—CO—CH}_3$

This was prepared in quantitative yield in the usual way by rubbing the amine with acetic anhydride. It was an oil.

14, Dimethyl-3,4, Dihydro-Isoquinoline [Cf Spath, 1930]



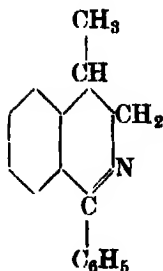
The acetyl derivative (4 g), dry toluene (16 c.c.) and phosphoryl chloride (10 c.c.) were heated and the product worked up in the usual way. The isoquinoline was obtained as an oil. Yield, 1.1 g (31 per cent of theory).

The *picrate* crystallised from alcohol in rhombic needles. M.P. 167°

*Benz-ββ, Phenyl Methyl Ethyl Amide*  
 $\text{C}_6\text{H}_5-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{NH}-\text{CO}-\text{C}_6\text{H}_5$

3.5 g of the amine gave 4.4 g of the benzoyl derivative crystallising from alcohol in thin needles M P  $85^\circ$

1, Phenyl-4, Methyl-3 4, Dihydro-Isoquinoline



This was obtained as an oil by heating 3 g of the benzoyl amide, 12 c c of dry toluene and 8 c c of phosphoryl chloride for two hours at  $110^\circ-120^\circ$ . The total weight of the dry base was 1.25 g, the yield being 45 per cent of that required by theory.

The *picate* prepared in the usual way crystallised from alcohol in rhombic needles M P  $150^\circ$

0.1198 g gave 13.5 c c of Nitrogen at  $30^\circ$  and 764 mm

Found N = 12.76 per cent

$\left. \begin{array}{l} \text{C}_{22}\text{H}_{18}\text{O}_7\text{N}_4 \\ (\text{C}_{16}\text{H}_{15}\text{N} \cdot \text{C}_6\text{H}_5\text{O}_7\text{N}_3) \end{array} \right\}$  requires N = 12.44 per cent

The *hydrobromide* was prepared by rubbing with 48 per cent HBr, drying the solid in an evacuated desiccator and crystallising from a mixture of alcohol and ether M P  $179^\circ-180^\circ$

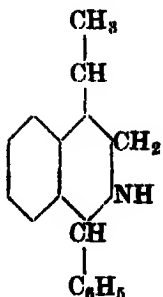
0.1700 g gave 0.1052 g AgBr

Found Br = 26.33 per cent

$\text{C}_{16}\text{H}_{15}\text{N}$ , HBr requires Br = 26.46 per cent

1, Phenyl-4, Methyl-1 2 3 4, Tetrahydro-Isoquinoline

The dihydro-isoquinoline (1.80 g) was reduced with zinc dust (4 g) and dilute sulphuric acid (30 c c) for 3-4 hours on a steam bath



After filtering and washing thoroughly with hot water to remove the isoquinoline sulphate adhering to the unreacted zinc, the liquid was basified strongly with caustic soda and the separated oil extracted thrice with benzene and worked up as before.

The isoquinoline was obtained as a white solid M P  $84^\circ-86^\circ$  Yield, 1.5 g

A small portion was crystallised from petroleum ether. The melting point remained unchanged.

0.1196 g gave 6.6 c c of Nitrogen at  $30^\circ$  and 765 mm

0.1125 g gave 0.3571 g of carbon dioxide and 0.0752 g of water

Found . C = 86.58; H = 7.43, N = 6.26 per cent

$\text{C}_{18}\text{H}_{17}\text{N}$  requires . C = 86.1, H = 7.62, N = 6.28 per cent

The *hydrochloride* was prepared by rubbing the base with concentrated HCl. It was sparingly soluble in water and hence easily crystallised from water. White rhombic needles. M P 244°

0.1676 g gave 0.0912 g AgCl.

Found Cl = 13.46 per cent

$C_{16}H_{17}N$ , HCl requires Cl = 13.68 per cent

The *hydrobromide* prepared in the same way crystallised in fine silky needles. M P 228°

*Phenyl Acet-ββ, Phenyl Methyl Ethyl Amide*  
 $C_6H_5-CH(CH_3)-CH_2-NH-CO-CH_2-C_6H_5$

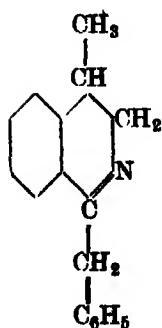
6 g of freshly prepared phenyl acetyl chloride was added slowly to a cold suspension of 3.3 g of the amine in 20 per cent caustic soda (20 c.c.). The separated amide was filtered and crystallised from alcohol. Yield, 5 g. M P 83°

0.1800 g gave 8.9 c.c. of nitrogen at 30° and 764 mm

Found N = 5.60 per cent

$C_{17}H_{19}ON$  requires N = 5.53 per cent

#### 1, Benzyl-4, Methyl-3, 4, Dihydro-Isoquinoline



1 g of the amide, 6 c.c. of toluene and 3 c.c. of phosphoryl chloride were worked up in the usual way and 0.35 g of the isoquinoline was formed as a basic oil.

The *picrate* crystallised from methanol in rhombic needles. M P. 169°

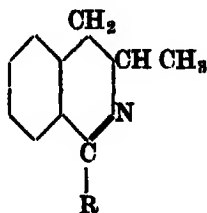
0.0952 g gave 10.4 c.c. of Nitrogen at 33° and 759 mm.

Found N = 12.18 per cent

$C_{23}H_{20}O_7N_4$   
 $(C_{17}H_{17}N.C_6H_5O_7N_3)$  } requires N = 12.07 per cent.

### SECTION C

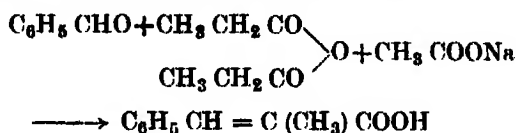
*Syntheses of 1, Substituted-3, Methyl-3, 4, Dihydro-Isoquinolines.*



(R =  $CH_3$ ,  $C_6H_5$  or  $C_6H_5.CH_3$ )

*α-Methyl Cinnamic Acid* —[Edeleano, 1887]  $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{COOH}$

This was prepared by Perkin's reaction from benzaldehyde, propionic anhydride and sodium acetate according to the following equations —



Benzaldehyde (23 g) propionic anhydride (30 g) and freshly fused and powdered sodium acetate (19.5 g) were heated in a flask fitted with an air condenser on an electric bath at  $130^\circ-135^\circ$  for 30 hours

The contents of the flask which had turned yellow were poured into 50 c.c. of water and treated with 4N caustic soda till it was alkaline and boiled for 5 minutes so as to convert all the acid into the sodium salt. The product was extracted with benzene (thrice with 30 c.c. each time) to remove unreacted benzaldehyde, etc., and the aqueous alkaline solution cooled in ice and acidified with concentrated HCl, the acid separating out almost completely as a white solid. The product was fairly pure and melted at  $73^\circ-74^\circ$ . Yield, 17.5 g

From the benzene extract 5 g of benzaldehyde were recovered by distillation

*α, Methyl-Hydro-cinnamic Acid* —[Rupe, 1909]

17.5 g of the cinnamic acid, reduced with 450 g of 4 per cent sodium amalgam, gave 17 g of the propionic acid as a high boiling liquid

*α, Methyl-β, Phenyl Propionamide*  $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CO}-\text{NH}_2$

Edeleano (1887) prepared the amide by heating the ammonium salt of the above acid

The dry acid (17 g) was converted into the acid chloride by warming with thionyl chloride in the usual way and a solution of the chloride in dry benzene (15 c.c.) added drop by drop to 180 c.c. of liquor ammonia containing 2 g of caustic soda dissolved in it

The solid amide which soon separated was filtered and weighed 11.2 g. On concentrating the filtrate another 0.9 g of the amide was obtained. It crystallised from boiling water in fine silky needles. M.P.  $108^\circ$

*α, Methyl-β, Phenyl Ethyl Amine*  $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{NH}_2$

Hey (1930) prepared the amine by the reduction of benzyl methyl ketoxime. The amine has advantageously been prepared now in good yields by Hofmann's degradation using hypochlorite solution. It was obtained as a strong basic yellow oil by treating the amide (5 g) with fresh hypochlorite solution prepared from 75 c.c. of 10 per cent caustic soda and chlorine

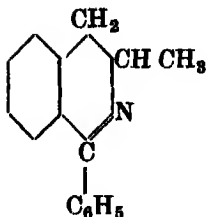


0.1955 g. gave 10.7 c.c. of Nitrogen at 31.5° and 755 mm

Found N = 6.1 per cent

$C_{16}H_{17}ON$  requires N = 5.9 per cent

1, Phenyl-3, Methyl-3, 4, Dihydro-Isoquinoline



1.5 g. of the isoquinoline was obtained as an oil from 4.3 g. of the amide by proceeding in the usual way. Yield, 35 per cent of that required by theory.

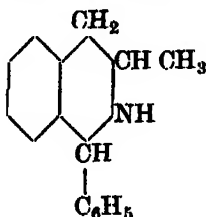
The *picrate* crystallised from alcohol in needles. M.P. 150°

0.1538 g. gave 17.5 c.c. of Nitrogen at 32.5° and 758 mm

Found N = 12.69 per cent

$C_{22}H_{18}O_7N_4$   
 $(C_{16}H_{15}N \cdot C_6H_3O_7N_3)$  } requires N = 12.44 per cent

1, Phenyl-3, Methyl-1, 2, 3, 4, Tetrahydro-Isoquinoline



0.8 g. of the tetrahydro base was obtained as an oil from 1 g. of the dihydro isoquinoline by reduction with zinc and sulphuric acid.

The *hydrobromide* crystallised from alcohol in fine silky needles. M.P. 230°-232°

0.2591 g. gave 0.1581 g. AgBr

Found Br = 25.96 per cent

$C_{16}H_{18}NBr$  requires Br = 26.29 per cent

The *hydrochloride* melted at 255°-256°

The *picrate* crystallised from dilute alcohol in needles. M.P. 161°

*Phenyl Acet-β, Phenyl-α, Methyl Ethylamide*  
 $C_6H_5-CH_2-CH(CH_3)-NH-CO-CH_2-C_6H_5$

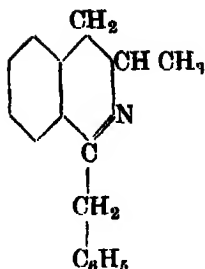
The amine (4 g.) was suspended in 20 per cent caustic soda (25 c.c.) cooled in ice and freshly made phenyl acetyl chloride (7 g.) was added slowly with vigorous stirring. The amide which separated as a solid was filtered and crystallised from alcohol in colourless needles. M.P. 114°. Yield, 6.5 g.

0.1806 g. gave 9.4 c.c. of Nitrogen at 33° and 762 mm.

Found N = 5.56 per cent

$C_{17}H_{19}ON$  requires N = 5.53 per cent

## 1, Benzyl-3, Methyl-3, 4, Dihydro-Isoquinoline



1.5 g of the amide, 6 c.c. of toluene and 4 c.c. of phosphoryl chloride heated in an oil bath at 110°–120° for 2 hours gave 0.6 g of the isoquinoline as a basic oil. Yield, 45 per cent.

The *picrate* crystallised from alcohol in rhombic needles. M.P. 139°.

0.1182 g of the *picrate* gave 12.8 c.c. of Nitrogen at 32° and 762 mm.

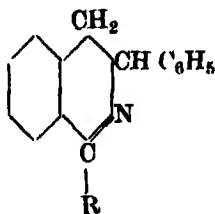
Found N = 12.18 per cent

$C_{23}H_{20}O_7N_4$  } requires N = 12.07 per cent  
 $(C_{17}H_{17}N C_6H_5O_7N_3)$

The *hydrobromide* prepared by rubbing the base with concentrated HBr crystallised from a mixture of alcohol and ether in thin needles. M.P. 225°.

## SECTION D

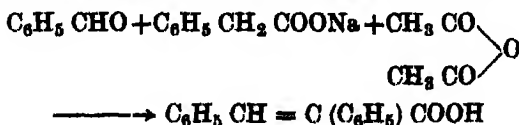
Attempt to synthesise 1, Substituted-3, Phenyl-3, 4, Dihydro-Isoquinolines.



(R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>5</sub> CH<sub>2</sub>)

α, Phenyl-cinnamic Acid C<sub>6</sub>H<sub>5</sub>–CH = C(C<sub>6</sub>H<sub>5</sub>)–COOH  
 [Oghaloro, 1878, Bakunin, 1897, 1901]

This was prepared by Perkin's synthesis from Benzaldehyde, sodium phenyl acetate and acetic anhydride according to the following equation —



Dry sodium phenyl acetate (28 g) was prepared by dissolving phenyl acetic acid (25 g) in sodium carbonate solution (40 c.c. containing 7.8 g sodium carbonate) evaporating to about 1/5 the volume, collecting the sodium salt on a filter, drying and fusing in a nickel crucible. This was mixed with benzaldehyde (19 g) and acetic anhydride (45 g) in a flask fitted with an air condenser and an inlet tube for passing CO<sub>2</sub>. It was heated on an oil bath for 6 hours at 190°–200° in an atmosphere of CO<sub>2</sub> and then poured on to crushed ice (100 g). The contents of the flask in which a solid had separated were steam distilled to remove unreacted benzaldehyde, of which there was

very little, the flask cooled and the solid filtered and washed with water (Filtrate A).

The solid was treated with cold dilute caustic soda, and filtered from a little insoluble matter (B). On acidifying with strong HCl, the  $\alpha$ , phenyl cinnamic acid was completely precipitated. Yield, 25 g.

It crystallised from hot glacial acetic acid in needles. M P  $170^\circ$ , identical with trans- $\alpha$ , phenyl-cinnamic acid.

Acidification of filtrate 'A' led to the precipitation of 2 g of a white substance which crystallised from hot acetic acid in thin plates. M P  $138^\circ$ . It proved to be the cis- $\alpha$  phenyl cinnamic acid.

The insoluble matter in caustic soda 'B' crystallised from hot acetic acid in rhombs. M P  $125^\circ$ . It was identified as stilbene. Yield, 3.2 g.

Result —

Trans- $\alpha$ , phenyl cinnamic acid	. 25 g
Cis- $\alpha$ , phenyl cinnamic acid	2 g
Stilbene	. 3.2 g

$\alpha$ , Phenyl Hydro-cinnamic Acid  $C_6H_5-CH_2-CH(C_6H_5)-COOH$

Cinnamic acid (15 g) reduced with 300 g of amalgam, gave the propionic acid as a white solid melting at  $82^\circ$ . Yield, 14 g.

$\alpha$ ,  $\beta$ , Diphenyl Propionamide.  $C_6H_5-CH_2-CH(C_6H_5)-CO-NH_2$   
[Mayer, 1888]

The dry acid (14 g) was converted into the acid chloride by warming with thionyl chloride (15 c.c.) in the usual way and a solution of the acid chloride in dry benzene (10 c.c.) was added drop by drop to liquor ammonia (200 c.c.). The solid amide was filtered and dried. M P  $131^\circ$ . Yield, 12.5 g.

$\alpha$ ,  $\beta$ , Diphenyl Ethyl Amine  $C_6H_5-CH_2-CH(C_6H_5)-NH_2$

Leuckart and Janssen (1889) have prepared the amine by heating desoxybenzoin and ammonium-formate and working up the reaction product in the usual way.

Here the amine was obtained as a liquid by Hofmann's reaction by treating the amide (5 g) with fresh hypochlorite solution prepared from 75 c.c. of 10 per cent caustic soda and chlorine generated from potassium permanganate (2.1 g) and working up the product in the usual way.

Acet- $\alpha\beta$ , Diphenyl Ethyl Amide  $C_6H_5-CH_2-CH(C_6H_5)-NH-CO-CH_3$   
[Leuckart (*loc cit*)]

It was prepared in quantitative yield by rubbing the amine (2.1 g) with acetic anhydride. It crystallised from hot alcohol in fine silky needles. M P  $148^\circ$ .

Cyclisation of the amide with phosphoryl chloride in toluene did not proceed at all.

*Benz-αβ, Diphenyl Ethyl Amide*  $C_6H_5-CH_2-CH(C_6H_5)-NH-CO-C_6H_5$   
[Leuckart (*loc cit*) ]

This was prepared in quantitative yield from the amine and benzoyl chloride by shaking with alkali. It crystallised from alcohol in fine needles M P  $176^\circ$

As in the case of the acetyl derivative, cyclisation did not proceed at all with the benzoyl derivative also

*Phenyl Acet-α, β, Diphenyl Ethyl Amide*  
 $C_6H_5-CH_2-CH(C_6H_5)-NH-CO-CH_3-C_6H_5$

The amine (31 g) was suspended in 10 per cent caustic soda (10 c.c.) cooled in ice and freshly prepared phenyl acetyl chloride (4 g) was added drop by drop with stirring. The amide which separated as a white solid was filtered, washed with water and crystallised from alcohol in thin needles Yield, 2.9 g M P  $182^\circ$

0.1887 g gave 7.6 c.c. of Nitrogen at  $33^\circ$  and 761 mm

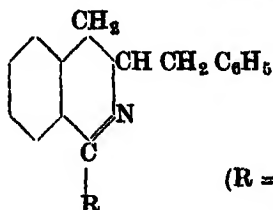
Found N = 4.5 per cent

$C_{22}H_{21}ON$  requires N = 4.44 per cent

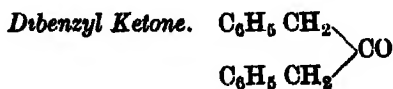
All attempts to cyclise the above amide to the corresponding isoquinoline, also failed as in the previous cases

## SECTION E

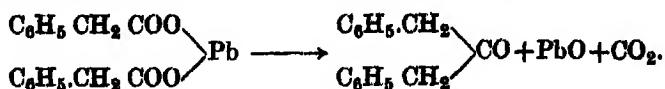
*Syntheses of 1, Substituted-3, Benzyl-3 4, Dihydro-Isoquinolines*



(R =  $CH_3$ ,  $C_6H_5$  or  $C_6H_5CH_2$ )



Young (1891) and Apitzsch (1904) prepared the ketone by the distillation of the dry calcium salt of phenyl acetic acid. The method of Kennern and Morton (1939) has been found to be more convenient and so employed here



The dry lead salt of phenyl acetic acid (43 g) prepared from sodium phenyl acetate and lead nitrate by double decomposition, was taken in a 100 c.c. distilling flask fitted with a thermometer and heated on a sand bath with a



potassium carbonate and the benzene distilled off. The amine which was obtained as an oil solidified on keeping in a desiccator. Yield, 6.5 g. M.P. 41°

In another experiment starting with 13 g. of the ketone 12 g. of the amine hydrochloride was obtained.

The *hydrochloride*\* crystallised from alcohol-ether mixture in fine needles. M.P. 202°

The *picrate*\* of the amine prepared in the usual way crystallised from hot alcohol in golden yellow plates. M.P. 193°

0.1072 g. of the picrate gave 12.2 c.c. of Nitrogen at 33° and 762 mm.

Found N = 12.74 per cent

$\left. \begin{array}{l} \text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_7 \\ (\text{C}_{15}\text{H}_{17}\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3) \end{array} \right\} \text{ requires N} = 12.73 \text{ per cent}$

The formyl derivative\* of the amine was easily soluble in alcohol and benzene. It crystallised from hot ligroin in fine silky needles. M.P. 90°

0.1477 g. of the substance gave 7.6 c.c. of Nitrogen at 28.5° and 757.2 mm.

Found N = 5.81 per cent

$\text{C}_{16}\text{H}_{17}\text{ON}$  requires N = 5.85 per cent

#### *Acet- $\alpha$ , Benzyl- $\beta$ , Phenyl Ethyl Amide*



The acetylated product (2.1 g.) was obtained by rubbing the amine (2.5 g.) with acetic anhydride. It was easily soluble in methanol, ethyl alcohol and benzene. It crystallised from ligroin in thin needles. M.P. 108°

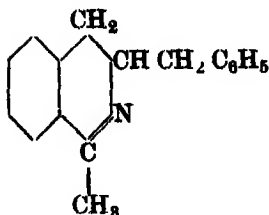
0.1596 g. gave 8.1 c.c. of Nitrogen at 33° and 760 mm.

Found N = 5.66 per cent

$\text{C}_{17}\text{H}_{19}\text{NO}$  requires N = 5.53 per cent

#### *1, Methyl-3, Benzyl-3, 4, Dihydro-Isoquinoline*

The amide (1 g.) was mixed with dry toluene (7 c.c.) and phosphoryl chloride (3 c.c.) in a small flask and heated at 115°–120° for two hours on an oil bath. The product was worked up in the usual way. 0.35 g. of isoquinoline (38 per cent of theory) was obtained as an oil.



The *picrate* prepared in the usual way crystallised from alcohol in yellow plates. M.P. 148°.

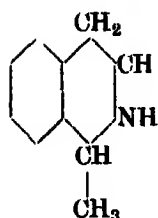
0.1053 g. gave 11.4 c.c. of Nitrogen at 33° and 760 mm.

\* S. Rajagopalan (*loc cit*)

Found N = 12.09 per cent  
 $\left. \begin{array}{l} \text{C}_{23}\text{H}_{20}\text{O}_7\text{N}_4 \\ (\text{C}_{17}\text{H}_{17}\text{N C}_6\text{H}_5\text{O}_7\text{N}_3) \end{array} \right\}$  requires N = 12.06 per cent

It was not possible to prepare the hydrochloride as it was very readily soluble in water.

### 1, Methyl-3, Benzyl-1, 2, 3, 4, Tetrahydro-Isoquinoline



The dihydro isoquinoline (1 g) was reduced with dilute sulphuric acid 20 c.c. and zinc dust (3 g) by heating on a water bath for three hours. The solution was filtered hot and the filtrate strongly basified with caustic soda, extracted with benzene, dried over potassium carbonate and the benzene distilled off. The isoquinoline was obtained as an oil weighing 0.9 g.

The hydrochloride prepared by rubbing the isoquinoline with concentrated HCl, drying in the desiccator, crystallised from alcohol-ether mixture in thin plates. M.P. 219°.

0.1112 g gave 0.0580 g of AgCl

Found Cl = 12.91 per cent

$\text{C}_{17}\text{H}_{19}\text{N HCl}$  requires Cl = 12.98 per cent

The hydrobromide prepared in the same way with concentrated HBr crystallised from alcohol-ether mixture in thin plates. M.P. 204°.

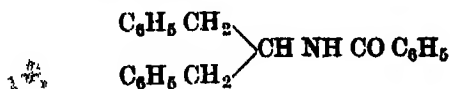
The picrate crystallised from methanol in rectangular plates. M.P. 160°-161°.

0.0784 g of the picrate gave 8.3 c.c. of Nitrogen at 33° and 761 mm

Found N = 11.83 per cent

$\left. \begin{array}{l} \text{C}_{23}\text{H}_{22}\text{O}_7\text{N}_4 \\ (\text{C}_{17}\text{H}_{19}\text{N C}_6\text{H}_5\text{O}_7\text{N}_3) \end{array} \right\}$  requires N = 12.01 per cent

### Benz- $\alpha$ , Benzyl- $\beta$ , Phenyl Ethyl Amide



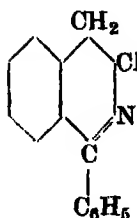
The amine (3 g.) on benzoylation by the Schotten-Baumann method yielded the benzoyl derivative (2.5 g) which crystallised from hot alcohol in thin needles. M.P. 166°.

0.1594 g gave 6.2 c.c. of Nitrogen at 33° and 761 mm

Found N = 4.35 per cent

$\text{C}_{22}\text{H}_{21}\text{NO}$  requires N = 4.44 per cent

## 1, Phenyl-3, Benzyl-3 4, Dihydro-Isoquinoline



The amide (1 g) dry toluene (6 c c) and phosphoryl chloride (3 c c) were taken in a small flask and heated on an oil bath for two hours at 115°-120° and the product worked up as usual

The isoquinoline (0.1 g 11 per cent of theory) was obtained as an oil

The *hydrochloride* prepared in the usual way and crystallised from absolute alcohol-ether mixture, melted at 143°

0.1030 g gave 0.0451 g of AgCl

Found Cl = 10.84 per cent

$C_{22}H_{19}N$  HCl requires Cl = 10.64 per cent

The *picrate* prepared by the usual method crystallised from alcohol in rhombs M P 172°

0.0718 g gave 6.8 c c Nitrogen at 33° and 758 mm

Found N = 10.57 per cent

$C_{28}H_{22}O_7N_4$   
 $(C_{22}H_{19}N \cdot C_6H_5O_3N_3)$  } requires N = 10.64 per cent

Phenyl Acet- $\alpha$ , Benzyl- $\beta$ , Phenyl-Ethyl Amide

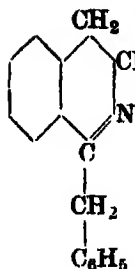
The amine (5 g) was suspended in 10 per cent caustic soda (15 c c) cooled in ice and phenyl acetyl chloride (6 g) was added drop by drop with vigorous shaking. Excess of alkali was finally added. The amide was filtered and washed free of alkali. It crystallised from alcohol in fine needles. Yield 4.3 g M P 134°

0.1534 g gave 5.8 c c of Nitrogen at 29° and 757 mm

Found N = 4.26 per cent

$C_{23}H_{23}ON$  requires N = 4.26 per cent

## 1, Benzyl-3, Benzyl-3 4, Dihydro-Isoquinoline



The amide (1 g) was mixed with dry toluene (7 c c) and phosphoryl chloride (3 c c) in a small flask and heated 115°-120° for two hours on an oil bath and the product worked up in the usual way

The isoquinoline (0.2 g 22 per cent of theory), was obtained as an oil

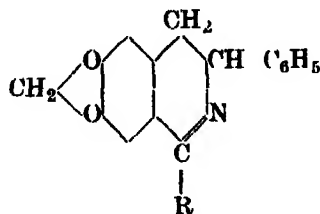
The *picrate* was crystallised from methyl alcohol M P 171°

0.1177 g gave 10.9 c c of Nitrogen at 29° and 758 mm.

Found N = 10.44 per cent  
 $\left. \begin{array}{l} \text{C}_{29}\text{H}_{24}\text{N}_4\text{O}_7 \\ (\text{C}_{28}\text{H}_{21}\text{N} \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7) \end{array} \right\}$  requires N = 10.37 per cent

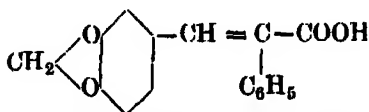
## SECTION F

*Syntheses of 1, Substituted 3, Phenyl-6 7, Methylene  
 Dioxy-3 4, Dihydro-Isoquinolines*



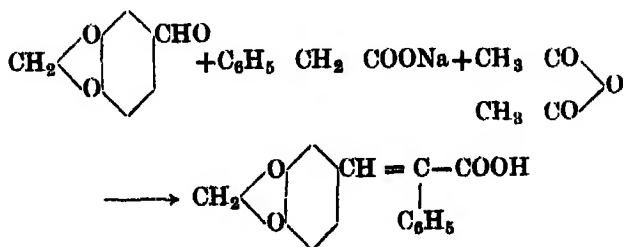
(R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)

*α, Phenyl Piperonyl Acrylic Acid*



[Dey and Krishna Rao, 1925]

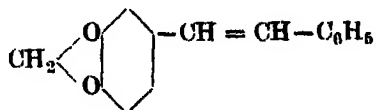
This was prepared by condensing piperonal with sodium phenyl acetate in presence of acetic anhydride, thus —



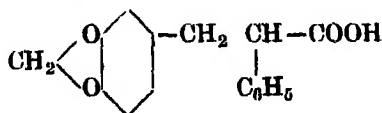
Piperonal (20 g), fused sodium phenyl acetate (22 g) and acetic anhydride (35 c c) were taken in a 200 c c bolt-head flask and heated on an oil bath at 160°–170° for 6 hours. The reaction product was cooled and the excess of acetic anhydride decomposed by adding water. The solid that separated was filtered and triturated with dilute caustic soda and the solution filtered off from a little solid (A) which remained undissolved. The filtrate was once extracted with benzene to remove other impurities, acidified with strong HCl and the precipitated acid filtered and washed. Yield, 23.7 g.

The crude acid (1 g) on crystallising from glacial acetic acid, yielded 0.7 g of the pure acid in rhombic needles M P  $232^{\circ}$

The portion insoluble in caustic soda (A) crystallised from glacial acetic acid in colourless needles Yield, 3.1 g M P  $97^{\circ}$  This was identified as 3,4-methylene dioxy stilbene



*$\alpha$ , Phenyl Piperonyl Propionic Acid*



The above acrylic acid (23 g) was dissolved in water (300 c.c.) containing caustic soda (3 g) and reduced with sodium amalgam (400 g of 4 per cent strength) in the usual way

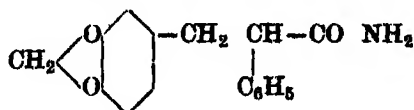
The propionic acid which came down as a sticky solid became gritty on rubbing. It was filtered, washed with water and crystallised from glacial acetic acid in needles Yield, 17 g M P  $125^{\circ}$

0.1236 g gave 3246 g of carbon dioxide and 0.532 g of water

Found C = 71.6, H = 5.18 per cent

$C_{16}H_{14}O_4$  requires C = 71.1, H = 5.10 per cent

*$\alpha$ , Phenyl- $\beta$ , Piperonyl Propionamide*



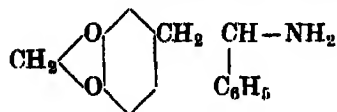
The dry propionic acid (13 g) and thionyl chloride (13 c.c.) were mixed in a 100 c.c. round bottomed flask and warmed on a water bath at  $90^{\circ}$  taking the usual precautions. After removing the excess of thionyl chloride under reduced pressure, the residual acid chloride was dissolved in 10 c.c. of dry benzene and added on to liquor ammonia (150 c.c.). The amide separated as a white solid which, on drying, weighed 12.5 g

The above amide (1 g) on crystallising from benzene, yielded 0.7 g of the pure amide in thin needles M P  $141^{\circ}$

0.1402 g gave 6.6 c.c. of Nitrogen at  $30.5^{\circ}$  and 756.5 mm

Found N = 5.27 per cent

$C_{16}H_{16}ON$  requires N = 5.20 per cent.

$\alpha$ , Phenyl Homopiperonyl Amine

A solution of sodium hypochlorite was prepared by passing chlorine gas generated from potassium permanganate (21 g) and hydrochloric acid into an ice cooled solution of 10 per cent sodium hydroxide (70 c.c.)

The finely powdered amide 5 g was added to the hypochlorite solution and vigorously shaken. The amide dissolved on warming. After keeping the solution at 70° for two hours solid potassium hydroxide (15 g) was added and heated to 80° at which temperature it was maintained for 45 minutes. The amine was extracted with benzene and the benzenic layer shaken with dilute hydrochloric acid. The acid layer was basified and extracted with ether, dried over potassium carbonate and the ether distilled off. The residual oil was then distilled under reduced pressure, the fraction coming between 260°–262° under 55 mm being collected. Yield, 2.4 g.

The *hydrochloride* of the amine crystallised from alcohol-ether mixture in fine needles. M.P. 239°–240°.

0.1467 g gave 0.738 g of AgCl

Found Cl = 12.47 per cent

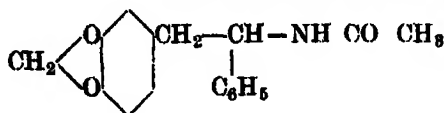
$C_{15}H_{16}NO_2Cl$  requires Cl = 12.77 per cent

The *picrate* crystallised from alcohol in rectangular plates. M.P. 192°.

0.0992 g gave 10.5 c.c. of Nitrogen at 31° and 757.5 mm

Found N = 11.85 per cent

$C_{21}H_{18}N_4O_9 =$   
 $(C_{15}H_{15}NO_2 \cdot C_6H_3N_3O_7) \}$  requires N = 11.91 per cent

*Acet- $\alpha$ , Phenyl- $\beta$  (3,4, Methyleneedioxy) Phenyl Ethyl Amide*

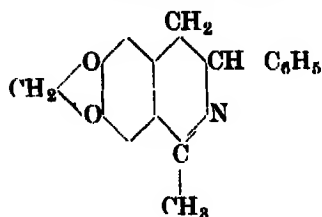
The amide was obtained in quantitative yield by rubbing the amine with acetic anhydride in a china dish. It crystallised from alcohol in thin needles. M.P. 141°.

0.1276 g gave 5.5 c.c. of Nitrogen at 30 and 757.5 mm

Found N = 4.86 per cent

$C_{17}H_{17}NO_3$  requires N = 4.94 per cent

## 1, Methyl-3, Phenyl-6 7, Methylenedioxy 3 4, Dihydro-Isoquinoline



A mixture of the amide (1 g), dry toluene (6 c c) and phosphoryl chloride (3 c c) was heated on an oil bath at  $120^\circ$  for two hours and the product worked up in the usual way 0.55 g of the isoquinoline (60 per cent of theory) was obtained as an oil

The *picrate* prepared in the usual way crystallised from hot alcohol in thin plates M P  $208^\circ$

0.1008 g gave 10.3 c c of Nitrogen at  $31^\circ$  and 760.2 mm

Found N = 11.48 per cent

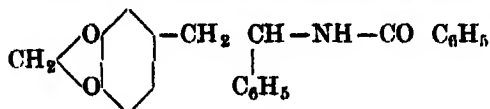
$\left. \begin{array}{l} \text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_9 \\ (\text{C}_{17}\text{H}_{15}\text{NO}_2 \text{ C}_6\text{H}_3\text{N}_3\text{O}_7) \end{array} \right\}$  requires N = 11.33 per cent

*Methiodide* 2 g of the isoquinoline and 1 c c of methyl iodide were mixed together and allowed to stand for 24 hours in a corked test tube. The yellow solid that had separated crystallised from absolute alcohol in golden yellow needles M P  $229^\circ$

0.1082 g gave 0.0624 g of silver iodide

Found I = 31.18 per cent.

$\text{C}_{18}\text{H}_{18}\text{NO}_2\text{I}$  requires I = 31.19 per cent

*Benz- $\alpha$ , Phenyl- $\beta$  (3 4, Methylenedioxy), Phenyl Ethyl Amide*

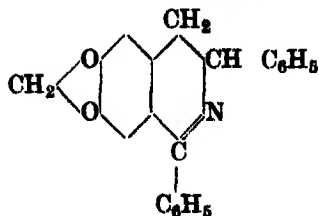
This was prepared in quantitative yield by shaking the amine with benzoyl chloride in presence of sodium hydroxide. It crystallised from alcohol in needles M.P.  $182^\circ$

0.1243 g gave 4.5 c c of Nitrogen at  $31^\circ$  and 759 mm

Found N = 4.06 per cent

$\text{C}_{23}\text{H}_{19}\text{NO}_2$  requires N = 4.18 per cent

## 1 3, Diphenyl-6 7, Methylenedioxy 3 4, Dihydro-Isoquinoline



A mixture of the benzamide (1 g), dry toluene (12 c c) and phosphoryl chloride (3 c c) was heated on an oil bath at  $120^\circ$  for two hours and the product worked up in the usual way. 0.25 g of the isoquinoline (28 per cent of theory) was obtained as a solid. It crystallised from alcohol in hexagonal plates M.P.  $146^\circ$ .

0.1072 g gave 0.3153 g of carbon dioxide and 0.0458 g of water  
 0.1123 g gave 4.2 c.c. of Nitrogen at 31° and 759 mm

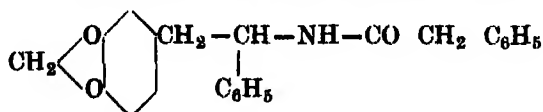
Found C = 80.21, H = 4.75, N = 4.16 per cent  
 $C_{23}H_{17}O_2N$  requires C = 80.71, H = 5.19, N = 4.28 per cent

The *picrate* of the isoquinoline crystallised from alcohol in rhombic needles  
 M.P. 172°

0.1096 g of the *picrate* gave 9.7 c.c. of Nitrogen at 31° and 759 mm  
 Found N = 9.93 per cent

$C_{28}H_{20}N_4O_9$   
 $(C_{23}H_{17}NO_2 \cdot C_6H_5N_3O_7)$  } requires N = 10.07 per cent

*Phenyl Acet- $\alpha$ , Phenyl- $\beta$  (3,4-Methylenedioxy), Phenyl Ethyl Amide*

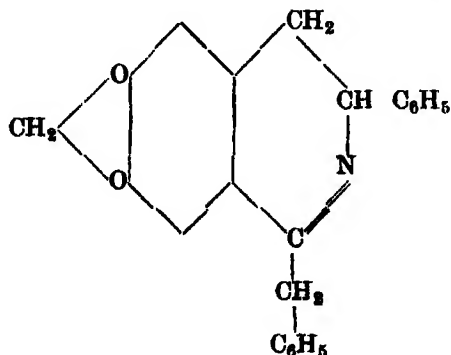


The amine (3 g) was suspended in 10 per cent sodium hydroxide (15 c.c.) cooled in ice and phenyl acetyl chloride (4 g) was added drop by drop with stirring. The amide was filtered and crystallised from hot alcohol in thin needles. Yield, 3 g. M.P. 185°

0.1468 g gave 4.9 c.c. of Nitrogen at 32° and 759 mm

Found N = 3.73 per cent  
 $C_{23}H_{21}O_2N$  requires N = 3.90 per cent

1, Benzyl-3, Phenyl-6,7, Methylenedioxy-3,4, Dihydro-Isoquinoline



The amide (1 g) dry toluene (10 c.c.) and phosphoryl chloride 3 c.c. were taken in small flask and heated on an oil bath at 120° for two hours. The reaction product was worked up in the usual way. 0.45 g (46 per cent of theory) of the isoquinoline was obtained as a solid. It was easily oxidised by air and could not be crystallised.

The *hydrochloride* prepared in the usual way crystallised from alcohol-ether mixture in thin needles M P  $176^{\circ}$  (decom)

0.1140 g gave 0.0432 g of AgCl

Found Cl = 9.38 per cent

$C_{23}H_{19}NO_2HCl$  requires Cl = 9.40 per cent

The *methiodide* crystallised from absolute alcohol in fine needles M P  $205^{\circ}$

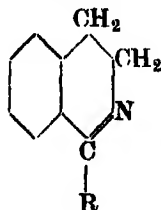
0.1076 g gave 0.0521 g of silver iodide

Found I = 26.16 per cent

$C_{24}H_{22}NO_2I$  requires I = 26.28 per cent

### SECTION G

#### *Syntheses of 1, Substituted-3, 4, Dihydro-Isoquinolines*

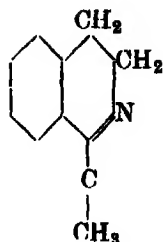


(R =  $CH_3$ ,  $C_6H_5$  or  $C_6H_5CH_2$ )

*Acet-β, Phenyl Ethyl Amide*  $C_6H_5CH_2CH_2NHCOCH_3$   
[Michaelis and Jacobi, 1893]

It was obtained in quantitative yield by rubbing β, phenyl ethyl amine with acetic anhydride. M P  $45^{\circ}$

#### *1, Methyl-3, 4, Dihydro-Isoquinoline*



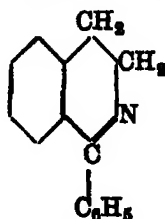
Pictet and Kay (1909), Spath and Co-workers (1930)

The acet-amide (1 g) dry toluene (5 c c) and phosphoryl chloride (3 c c) were heated on an oil bath at  $115^{\circ}$ – $120^{\circ}$  for 2 hours and the product worked up in the usual way 0.21 g. of the isoquinoline (22 per cent of theory) was obtained as an oil. The picrate crystallised from alcohol in needles M.P.  $189^{\circ}$

*Benz-β, Phenyl Ethyl Amide*  $C_6H_5-CH_2-CH_2-NH-CO-C_6H_5$   
[Michaelis (*loc cit*)]

It was prepared in quantitative yield by shaking β Phenyl ethyl amine with benzoyl chloride in the presence of alkali. It crystallised from alcohol M P  $115^{\circ}$

## 1, Phenyl-3·4, Dihydro-Isoquinoline

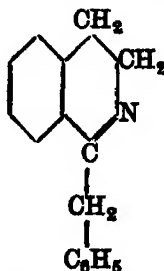
[Decker and Kropp (1909), Spath and Co-workers (*loc cit*) ]

A mixture of the benz-amide (1 g ), dried toluene (5 c c ) and phosphoryl chloride (3 c c ) were taken in a small flask and heated on an oil bath at 115°-120° for 2 hours and the product worked up as usual 0.25 g (26 per cent of theory), of the isoquinoline was obtained as an oil The picrate crystallised from alcohol in long needles M P 174°

*Phenyl Acet-β, Phenyl Ethyl Amide*[Decker and Kropp (*loc cit*) ]

The amine (1.5 g ) was suspended in sodium hydroxide (10 c c ) of 10 per cent strength cooled in ice and phenyl acetyl chloride (2.3 g ) was added drop by drop stirring mechanically The amide crystallised from alcohol M P 94°

## 1, Benzyl-3·4, Dihydro-Isoquinoline

[Pictet and Kay (*loc cit.*), Spath and Co-workers (*loc cit* ).]

The amide (1 g ) on cyclising with phosphoryl chloride (3 c c ) in dry toluene (6 c.c.) under the above experimental conditions yielded 0.08 g of the isoquinoline (9 per cent of theory), as an oil The picrate crystallised from alcohol M.P 175°

## SUMMARY

The acet-, benz-, and phenyl acet- derivatives of (a) β, β, methyl, phenyl-ethyl amine, (b) α, β, methyl phenyl ethyl amine, (c) β, β, diphenyl ethyl amine, (d) α, β, benzyl phenyl ethyl amine and (e) α, phenyl β, (3·4, methylene dioxy)-

phenyl ethyl amine were prepared and cyclised to the corresponding 3,4 dihydro isoquinolines. The cyclisation of the acyl derivatives of  $\alpha$ , methyl- $\beta$ , phenyl ethyl amine, with the exception of the benz- derivative, has been found, as a rule, to be more facile than that of the corresponding derivatives of the  $\beta$ , methyl- $\beta$ , phenyl ethyl amine. Apart from this effect of the methyl group in the  $\alpha$ , and in the  $\beta$ , positions of the above-mentioned acyl amides, the acyl groups themselves have been observed to exert a considerable influence on the progress of the cyclisation. Thus, while the phenyl group in the  $\beta$ , position in the acetyl and phenyl acetyl-derivatives of  $\beta$ ,  $\beta$ , diphenyl ethyl amine is found to have little or no influence on the course of the reaction which proceeds normally, the benzoyl derivative of the same amine gave a much better yield of the isoquinoline. This increase is truly remarkable and brings into prominence the significance of the acyl radical also in respect of the ease or otherwise with which the ring is closed. The effect of the benzyl group is very similar, as is to be expected, to that of the methyl group, the acyl  $\alpha$ , benzyl  $\beta$ , phenyl ethyl amides being cyclised readily. Here, too, the same influence of the acyl group is witnessed, the acetyl derivative giving the highest and the benzoyl the lowest yield of the base. The retarding effect of the  $\alpha$ , phenyl group is illustrated in the case of the acyl  $\alpha$ ,  $\beta$ , diphenyl-ethyl amides which refused to cyclise at all under the usual conditions. The retardation was, however, overcome to a considerable extent by introducing a methylene dioxy group in the phenyl nucleus of the  $\beta$ -phenyl ethyl amine and activating the para hydrogen atom responsible for the cyclisation. Thus the acyl derivatives of  $\alpha$ , phenyl- homopiperonyl amine could be made to cyclise, while those of  $\alpha$ ,  $\beta$ , diphenyl ethyl amine failed to give even a trace of the isoquinoline. The isoquinolines have been characterised by their picrates, hydrochlorides, hydrobromides and methiodides. The dihydro isoquinolines in most cases have been reduced to the tetrahydro compounds and the picrates, hydrochlorides, hydrobromides and benzoyl derivatives of these tetrahydro isoquinolines have also been prepared.

PRESIDENCY COLLEGE

MADRAS

31st October, 1942

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# SOME NEW RELATIVISTIC DISTRIBUTIONS OF RADIAL SYMMETRY.

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(Received, October 27, 1942)

## ABSTRACT

Several new solutions, which are static and isotropic, of Einstein's field equations are obtained. The inadequacy of the usual boundary conditions is brought to light. Following Tolman's treatment of the subject it is shown that certain expressions are tacitly assumed to be continuous on the boundary. For the particular case of static isotropic solutions of radial symmetry the new condition is the continuity of  $\mu'$ . The examples given have possible astronomical interest and they bring out the efficacy of the new condition.

## INTRODUCTION

Following some recent work by Tolman (1939) we have discussed in a series of communications\* the solutions of Einstein's field equations for spheres of fluid of the form,

$$ds^2 = -e^\lambda dr^2 - r^2(d\theta^2 + \sin^2\theta d\phi^2) + e^\nu dt^2 \quad (1)$$

$$\lambda = \lambda(r), \nu = \nu(r).$$

We have also gone into the question of boundary conditions and brought to light a new necessary condition. In this paper we consider solutions of the form,

$$ds^2 = -e^\mu(dr^2 + r^2d\theta^2 + r^2\sin^2\theta d\phi^2) + e^\nu dt^2 \quad (2)$$

$$\mu = \mu(r), \nu = \nu(r).$$

Obviously, (1) and (2) are transformable into each other. The physical content of (2) cannot, therefore, be different from that of (1). The object in choosing the other co-ordinate system is this. The form of the differential equations in  $\mu$  and  $\nu$  suggests some new particular solutions which are not quite obvious from the differential equations arising from (1). The results of the next section will bear this out.

For the line-element (2) the non-zero components of the energy-momentum tensor are

$$8\pi T_1^1 = -8\pi p = -e^{-\mu} \left( \frac{\mu'^2}{4} + \frac{\mu'\nu'}{2} + \frac{\mu' + \nu'}{r} \right) - \Lambda, \quad (3)$$

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\* Two letters are recently published in *Current Science* and a paper is in the press with the *Journal of the Bombay University* — V V N (7-7-1943)

$$8\pi T_2^2 = 8\pi T_3^3 = -8\pi q = -e^{-\mu} \left( \frac{\mu''}{2} + \frac{\nu''}{2} + \frac{\nu'^2}{4} + \frac{\mu' + \nu'}{2r} \right) - \Lambda, \quad (4)$$

$$8\pi T_4^4 = 8\pi p = -e^{-\mu} \left( \mu'' + \frac{\mu'^2}{4} + \frac{2\mu'}{r} \right) - \Lambda \quad (5)$$

Here and in what follows a dash denotes a differentiation with regard to  $r$  as in  $\mu'$ . For fluid spheres of stellar dimensions the cosmological constant  $\Lambda$  can be safely neglected. For the pressure to be isotropic it is necessary that  $p = q$  or

$$\mu'' + \nu'' + \frac{\nu'^2 - \mu'^2}{2} - \mu'\nu' - \frac{\mu' + \nu'}{r} = 0 \quad (6)$$

Let us now consider the particular solutions arising out of the last equation

#### NEW PARTICULAR SOLUTIONS

The equation of isotropy (6) can be expressed as

$$z'' - z' \left( \mu' + \frac{1}{r} \right) + z \left( \frac{\mu''}{2} - \frac{\mu'^2}{4} - \frac{\mu'}{2r} \right) = 0, \quad (7)$$

where 
$$z = e^{\frac{\nu}{2}} \quad (8)$$

In our search of particular solutions we may start with the simplifying assumption,

$$\frac{\mu''}{2} - \frac{\mu'^2}{4} - \frac{\mu'}{2r} = \left( 1 - \frac{n^2}{4} \right) \frac{1}{r^2} \quad (9)$$

It leads to

$$e^{-\frac{\mu}{2}} = A_1 r^{1+\frac{n}{2}} + A_2 r^{1-\frac{n}{2}}, \quad (10.1)$$

$$e^{\frac{\nu}{2}} = \left( B_1 r^{1+\frac{x}{2}} + B_2 r^{1-\frac{x}{2}} \right) \left( A_1 r^{1+\frac{n}{2}} + A_2 r^{1-\frac{n}{2}} \right)^{-1}, \quad (10.2)$$

where 
$$x = (2n^2 - 4)^{\frac{1}{2}} \quad (11)$$

The pressure and density are given by

$$8\pi p = \frac{\left( B_1 r^{1+\frac{x}{2}} + B_2 r^{1-\frac{x}{2}} \right)^{-1}}{4} [(n-x)^2 \alpha + (n+x)^2 \beta - 2(3n^2 + 4)\gamma], \quad (10.3)$$

$$8\pi \rho = \left( 1 - \frac{n^2}{4} \right) A_1^2 r^n + 2A_1 A_2 \left( 1 + \frac{5}{4} n^2 \right) + A_2^2 \left( 1 - \frac{n^2}{4} \right) r^{-n}, \quad (10.4)$$

$$\text{where} \quad \alpha = A_1^2 B_1 r^{1+n+\frac{x}{2}} + A_2^2 B_2 r^{1-n-\frac{x}{2}}, \quad (12.1)$$

$$\beta = A_1^2 B_2 r^{1+n-\frac{x}{2}} + A_2^2 B_1 r^{1-n+\frac{x}{2}}, \quad (12.2)$$

$$\gamma = B_1 r^{1+\frac{x}{2}} + B_2 r^{1-\frac{x}{2}} \quad (12.3)$$

The constants  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$  are to be determined (Tolman, 1934*b*) as usual by using the conditions (i)  $p = 0$  at  $r = a$  and that (ii)  $g_{\mu\nu}$  are continuous at  $r = a$ . The external (Eddington, 1924) solution, valid for  $r > a$  is

$$ds^2 = -\left(1 + \frac{m}{2r}\right)^4 dr^2 - r^2 (d\theta^2 + \sin^2 \theta d\phi^2) + \left(\frac{1 - \frac{m}{2r}}{1 + \frac{m}{2r}}\right)^2 dt^2 \quad (13)$$

Thus (i) and (ii) provide only three conditions. We are showing in the next section that all the constants become known when we use the additional condition that  $\mu'$  is continuous at  $r = a$ . In all this  $a$  is taken as the radius of the material distribution. We have considered the fourth condition in a more detailed way elsewhere as it was never hinted at or used in such problems before. The significance of the new condition is this: it ensures that the total energy of the distribution (2) is the same as that of a particle of mass  $m$  so far as the field at great distances is concerned. Using the conditions we get

$$A_1 = -a^{-1+\frac{n}{2}} \frac{(2-n)-(2+n)\frac{m}{2a}}{2n\left(1+\frac{m}{2a}\right)^3}, \quad (14.1)$$

$$A_2 = a^{-1+\frac{n}{2}} \frac{(2+n)-(2-n)\frac{m}{2a}}{2n\left(1+\frac{m}{2a}\right)^3}, \quad (14.2)$$

$$B_1 = \frac{\frac{4m}{a} - (2-x) - (2+x)\frac{m^2}{4a^2}}{2x\left(1+\frac{m}{2a}\right)^4} a^{-1+\frac{x}{2}}, \quad (14.3)$$

$$B_2 = -\frac{\frac{4m}{a} - (2+x) - (2-x)\frac{m^2}{4a^2}}{2x\left(1+\frac{m}{2a}\right)^4} a^{-1+\frac{x}{2}} \quad (14.4)$$

For  $\rho$  to be non-negative  $n$  must not exceed 2 and for  $x$  to be real  $n$  cannot be less than  $\sqrt{2}$ . Thus the above solution is possible only if

$$2 > n > \sqrt{2} \quad (15)$$

and for  $n = \sqrt{2}$  we have

$$e^{-\frac{\mu}{2}} = A_1 r^{1+\frac{1}{\sqrt{2}}} + A_2 r^{1-\frac{1}{\sqrt{2}}} \quad (16.1)$$

$$e^{\frac{\nu}{2}} = \frac{B_1 + B_2 \log r}{A_1 r^{\frac{1}{\sqrt{2}}} + A_2 r^{-\frac{1}{\sqrt{2}}}}, \quad (16.2)$$

$$8\pi\rho = A_1^2 \left\{ \frac{1}{2} \left( r^{\frac{1}{\sqrt{2}}} - br^{-\frac{1}{\sqrt{2}}} \right)^2 - 4b - \sqrt{2} B_2 \frac{r^{\frac{1}{\sqrt{2}}} + br^{-\frac{1}{\sqrt{2}}}}{B_1 + B_2 \log r} \right\}, \quad (16.3)$$

$$8\pi\rho = A_1^2 \left[ \frac{1}{2} \left( r^{\frac{1}{\sqrt{2}}} + br^{-\frac{1}{\sqrt{2}}} \right)^2 + 6b \right], \quad (16.4)$$

where 
$$b = \frac{A_2}{A_1} \quad (17)$$

There is no change in the forms of  $A_1$  and  $A_2$  but the values of  $B_1$  and  $B_2$  now become

$$B_1 = \frac{1 - \frac{m}{2a}}{a \left( 1 + \frac{m}{2a} \right)^3} - \frac{\frac{m}{a} - \left( 1 - \frac{m}{2a} \right)^2}{a \left( 1 + \frac{m}{2a} \right)^4} \log a, \quad (18.1)$$

$$B_2 = \frac{\frac{m}{a} - \left( 1 - \frac{m}{2a} \right)^2}{a \left( 1 + \frac{m}{2a} \right)^4} \quad (18.2)$$

It can easily be verified that  $n = x = 2$  corresponds to Schwarzschild's solution in the isotropic form. For  $n < \sqrt{2}$  the forms of  $\mu$  and  $\rho$  are unchanged. But we have

$$e^{\frac{\nu}{2}} = \left( A_1 r^{\frac{n}{2}} + A_2 r^{-\frac{n}{2}} \right) r^2 \left[ B_1 \cos \left( \frac{x}{2} \log r \right) + B_2 \sin \left( \frac{x}{2} \log r \right) \right] \quad (19.1)$$

and

$$8\pi\rho = A_1^2 r^n \left\{ \frac{3}{4} n^2 - 1 + \frac{nx}{2} \tan \left( \frac{x}{2} \log r - \phi \right) \right\} - 2A_1 A_2 \left( 1 + \frac{3}{4} n^2 \right) + A_2^2 r^{-n} \left\{ \frac{3}{4} n^2 - 1 - \frac{nx}{2} \tan \left( \frac{x}{2} \log r - \phi \right) \right\} \quad (19.2)$$

where 
$$x = (4 - 2n^2)^{\frac{1}{2}}, \quad (20)$$

and 
$$\tan \phi = B_2/B_1 \quad (21)$$

Another solution, which is new and important and which brings out the inadequacy of the usual boundary conditions follows from the assumption

$$\mu' = \frac{k}{r}, \quad (22)$$

where  $k$  is a constant. From the assumption and the usual boundary conditions one gets

$$e^\mu = \left(1 + \frac{m}{2a}\right)^4 \left(\frac{r}{a}\right)^k, \quad (23.1)$$

$$e^{\frac{r}{2}} = \frac{1 - \frac{m}{2a}}{1 + \frac{m}{2a}} \frac{1}{2d} \left(\frac{r}{a}\right)^{1-n+\frac{k}{2}} \left[ (c+d) - (c-d) \left(\frac{r}{a}\right)^{2n} \right], \quad (23.2)$$

where 
$$c = 2 + 3k + \frac{3}{4} k^2, \quad (24.1)$$

$$d = n(k+2), \quad (24.2)$$

$$n = \left(1 + 2k + \frac{1}{2} k^2\right)^{\frac{1}{2}} \quad (24.3)$$

The density and pressure are given by the expressions

$$8\pi\rho = -\frac{a^k r^{-k-2}}{\left(1 + \frac{m}{2a}\right)^4} \left(k + \frac{k^2}{4}\right), \quad (23.3)$$

$$8\pi p = \frac{a^k (c^2 - d^2)}{\left(1 + \frac{m}{2a}\right)^4 r^{k+2}} \left[ \frac{a^{2n} - r^{2n}}{(c+d)a^{2n} - (c-d)r^{2n}} \right] \quad (23.4)$$

It is worthy of notice that

$$8\pi p' = -\frac{(k+2) r^{-k-3} a^k}{\left(1 + \frac{m}{2a}\right)^4 (1-y)^2} \left[ y + \frac{k + \frac{k^2}{4}}{c+d} \right]^2, \quad (25)$$

where 
$$y = \frac{c-d}{c+d} \left(\frac{r}{a}\right)^{2n}. \quad (26)$$

$\rho$  and  $p$  will be non-negative and  $n$  real provided

$$0 > k > -2 + \sqrt{2} \quad (27)$$

A solution thus obtained does not satisfy the additional criterion, which is the analogue of the Gauss theorem, that the field represented should be equivalent

to that of a particle of mass  $m$  at infinity. This is true only if  $\mu'$  is continuous which means the additional restraint, viz.,

$$\frac{m}{a} = -\frac{2k}{k+4} \quad \dots \quad (28)$$

In the case  $n = 0$ , the forms of  $v$  and  $p$  differ. We have

$$e^{\frac{v}{2}} = \frac{1 - \frac{m}{2a}}{1 + \frac{m}{2a}} \left(\frac{r}{a}\right)^{\frac{1}{\sqrt{2}}} \left[1 + \frac{\log a - \log r}{2\sqrt{2}}\right], \quad (29\ 1)$$

$$8\pi p = \frac{1}{2} a \frac{2 + \sqrt{2} r - \sqrt{2}}{\left(1 + \frac{m}{2a}\right)^4} \left[\frac{\log a - \log r}{\log a - \log r + 2\sqrt{2}}\right]. \quad (29\ 2)$$

This implies the particular relation,

$$\frac{m}{a} = \frac{4 - 2\sqrt{2}}{2 + \sqrt{2}} \quad (30)$$

In case  $n$  is not real we put

$$n_1 = \sqrt{-(1 + 2k + k^2/2)} \quad (31)$$

In this case also the forms of  $\mu$  and  $\rho$  are the same as before. Only  $v$  and  $p$  become different

$$e^{\frac{v}{2}} = \frac{1 - \frac{m}{2a}}{1 + \frac{m}{2a}} \sec \phi \left(\frac{r}{a}\right)^{1 + \frac{k}{2}} \cos [n_1 \log (r/a) + \phi], \quad (32\ 1)$$

$$8\pi p = \frac{n_1(k+2) a^{\frac{1}{2}} r^{-k-2}}{\left(1 + \frac{m}{2a}\right)^4} \left\{ \tan \phi - \tan [n_1 \log (r/a) + \phi] \right\}, \quad (32\ 2)$$

where  $\tan \phi = \frac{2 + 3k + 3k^2/4}{n_1(k+2)} \quad (33)$

For  $p$  and  $\rho$  to be non-negative it is necessary that

$$-2 + \sqrt{2} > k > -2 \quad (34)$$

It is worthy of notice that in all these cases  $p$  strictly diminishes from the centre to the surface without attaining a minimum

We will now present the considerations that have lead us to regard  $\mu'$  as continuous at  $r = a$

#### NEW CONTINUITY CONDITIONS ON THE BOUNDARY, $r = a$

If the material distribution represented by the internal solution

$$ds^2 = g_{\mu\nu} dx^\mu dx^\nu \quad (35)$$

is to behave like a particle of mass  $m$  at great distances it is required that the total energy of the system be  $m$ . In the exposition of this point Tolman (1934a) has tacitly assumed, among other things, the continuity of

$$-g^{\alpha 4} \sqrt{-g} A_{\mu\alpha}^{\gamma} + \frac{1}{2} g_{\mu}^4 g^{\alpha\beta} \sqrt{-g} A_{\alpha\beta}^{\gamma} \quad (36)$$

$$\mu = 1, 2, 3, 4, \quad \gamma = 1, 2, 3$$

on the boundary of the distribution. Here

$$A_{\alpha\beta}^{\gamma} = -\Gamma_{\alpha\beta}^{\gamma} + \delta_{\alpha}^{\gamma} \Gamma_{\beta\rho}^{\rho} + \delta_{\beta}^{\gamma} \Gamma_{\alpha\rho}^{\rho} \quad (37)$$

Let us see what this condition really amounts to for several familiar systems

Case (1)

$$g_{\mu\nu} = \delta_{\mu\nu} + h_{\mu\nu} \quad (38)$$

This is the case of a weak gravitational field,  $\delta_{\mu\nu}$  having the usual meaning and the squares of  $h$ 's being neglected. Here the continuity to be discussed is of

$$\begin{aligned} & \frac{1}{2} \delta^{\gamma\gamma} \left[ \frac{\partial h_{\mu\gamma}}{\partial x^4} + \frac{\partial h_{4\gamma}}{\partial x^{\mu}} - \frac{\partial h_{4\mu}}{\partial x^{\gamma}} \right] \\ & - \frac{1}{4} g_{\mu}^{\gamma} \frac{\partial}{\partial x^{\gamma}} [h_{44} - h_{11} - h_{22} - h_{33}] \\ & - \frac{1}{4} g_{4}^{\gamma} \frac{\partial}{\partial x^{\mu}} [h_{44} - h_{11} - h_{22} - h_{33}] \\ & - \frac{1}{4} g_{\mu}^4 \delta^{\alpha\alpha} \delta^{\gamma\gamma} \left( 2 \frac{\partial h_{\alpha\gamma}}{\partial x^{\alpha}} - \frac{\partial h_{\alpha\alpha}}{\partial x^{\gamma}} \right) \\ & + \frac{1}{4} g_{\mu}^4 \delta^{\gamma\gamma} \frac{\partial}{\partial x^{\gamma}} [h_{44} - h_{11} - h_{22} - h_{33}] \end{aligned} \quad (39)$$

[N.B.—In the above  $\gamma, \mu$  are real suffixes while  $\alpha$  is a 'dummy' suffix so far as the summation convention goes.]

From the above the twelve expressions corresponding to  $\mu = 1, 2, 3, 4$  and  $\gamma = 1, 2, 3$  can be easily obtained in concrete forms. If the cross terms  $h_{\mu\nu} = 0$  (when  $\mu \neq \nu$ ) the following six expressions are required to be continuous on the boundary of the distribution

$$\begin{aligned} (1) \quad & \frac{\partial}{\partial x^1} (h_{22} + h_{33}), & (2) \quad & \frac{\partial}{\partial x^4} (h_{44} + h_{11} - h_{22} - h_{33}), \\ (3) \quad & \frac{\partial}{\partial x^2} (h_{11} + h_{33}), & (4) \quad & \frac{\partial}{\partial x^4} (h_{44} - h_{11} + h_{22} - h_{33}), \\ (5) \quad & \frac{\partial}{\partial x^3} (h_{11} + h_{22}), & (6) \quad & \frac{\partial}{\partial x^4} (h_{44} - h_{11} - h_{22} + h_{33}). \end{aligned} \quad (40)$$

Case (ii)

$$ds^2 = -A(dx^1)^2 - B(dx^2)^2 - C(dx^3)^2 + D(dx^4)^2 \quad (41)$$

The continuity of the following six expressions is demanded on the boundary

$$\begin{aligned} (1) \quad & -\frac{A_4}{A} + \frac{B_4}{B} + \frac{C_4}{C} + \frac{D_4}{D}, & (2) \quad & \frac{B_1}{B} + \frac{C_1}{C}, \\ (3) \quad & \frac{A_4}{A} - \frac{B_4}{B} + \frac{C_4}{C} + \frac{D_4}{D}, & (4) \quad & \frac{A_2}{A} + \frac{C_2}{C}, \\ (5) \quad & \frac{A_4}{A} + \frac{B_4}{B} - \frac{C_4}{C} + \frac{D_4}{D}, & (6) \quad & \frac{A_3}{A} + \frac{B_3}{B} \end{aligned} \quad (42)$$

In the notation adopted in the above expressions a suffix denotes a differentiation with respect to the corresponding variable. Thus  $D_2 \equiv \partial D / \partial x^2$ .

Case (iii) For the line-element (1) which is a particular case of case (ii) no new condition is implied if  $\lambda$  and  $\nu$  are continuous. But for (2) the condition turns out to be that  $\mu'$  be continuous. Hence we understand how the usual boundary conditions are enough in the former case while they fall short of one in the latter. For (2) even  $\nu'$  is continuous. This has a deeper significance which we intend to consider in another paper.

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# ON THE FITTING OF AN ADIABATIC CORE TO A RADIATIVE ENVELOPE IN STELLAR MODELS

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## ABSTRACT

A method is discussed for the fitting of a convective core to a radiative envelope in stellar models in which the radiation pressure is not necessarily negligible. The problem has a solution only under certain restrictions. Curves are given which are expected to facilitate the fitting of solutions, when this is feasible.

## INTRODUCTION

Since the publication of Bethe's (1939) theory of energy generation in stellar interiors, attempts have been made for an accurate determination of the temperature density distribution in the main sequence stars which would be a necessary consequence of the proposed energy generation law. A comparison of such a model with empirical knowledge from observations is also expected to help us to make a decision regarding the correctness or otherwise of the energy generation law. For the present it is necessary to work out all models which may be built up from Bethe's hypothesis regarding the sources of stellar energy. In a previous paper (Burman, 1942) we have carried out some numerical integrations of the stellar equations on the assumption of Bethe's law of energy generation in its accurate form and radiative transfer of energy. For central conditions appropriate to the main sequence stars our integrations do not lead to a solution which may correspond to a stellar body configuration. The attempt would then naturally be to introduce a convective core at the centre, in which an adiabatic gradient will obtain, which would subsequently give place to a radiative gradient within an outer envelope. It appears that the solution cannot possibly start with a radiative gradient from the centre, as it has been shown by N R Sen (1941), that for such a strong temperature dependence of the energy generation as is demanded by Bethe's theory (in fact, also for a very much weaker temperature dependence), if the gradient at start is radiative, it will continue to remain such outwards all along. The possible stellar model will then have a convective core, allowing mixing of matter, with a radiative envelope surrounding it where the standard equations of radiative equilibrium will hold.

The suggestion of a convective core has been a long-standing one, and in fact the works of Rosseland, Cowling and others have clearly pointed to that necessity. In a recent paper Blanch, Lowan, Marshak and Bethe (1941) have worked out a model for the sun with an adiabatic core, inside which almost the whole energy generation takes place according to Bethe's law, surrounded by an envelope, in which a radiative gradient prevails and no further energy is generated. As the radiation pressure has been assumed to be negligible, the inner core is an Emden-polytrope of index  $n = 3/2$ . The luminosity, however, is unfortunately in error by a factor 100.

The general problem will be to integrate the stellar equations inwards from the surface of the star subject to the boundary conditions

$$\rho = 0$$

$$T = 0$$

$$M(r) = M \text{ (total mass), } L(r) = L \text{ (total luminosity)}$$

at  $r = R$  (boundary radius).

This solution is to be continued inwards until the radiative gradient gives place to an adiabatic one from which stage an adiabatic core may be supposed to begin, throughout this core the equations of convective equilibrium hold. The solution should be true to the inner boundary condition, viz  $M(r) = 0$ ,  $L(r) = 0$ , at  $r = 0$ . To study such a model it is necessary to have a more detailed knowledge, than we have at present, of the core in adiabatic equilibrium, which may be fitted on to a given radiative envelope and in which the radiation pressure is not necessarily negligible. As a result of integration from outside, the envelope is obtained as enclosing a definite mass of matter within a given radius where the pressure and density are also known. The integration will indeed also yield a luminosity for that radius but the adjustment of luminosity is to be tested by a separate process.

We set the problem we consider now, as follows —

Given the pressure, density and mass (obtained from integrations in the envelope starting from the stellar surface) at a certain radial distance, which defines the outer surface of a spherically symmetrical core in convective equilibrium, to find the adiabatic core (if it exists) which may be fitted on to this envelope, in other words we seek a solution of the equations of adiabatic equilibrium having these given values of pressure, density and mass at that particular radius and no singularity at the origin. The problem of the solution of the equations of convective equilibrium has already been considered by Biermann (1932). He has shewn generally how from a set of one parametric solutions, the parameter chosen being  $(1-\beta)$ , all possible solutions in the convective region may be obtained even when the radiation pressure is not negligible. For our present purpose we require, however, a much fuller set of one parametric solutions of the equations of convective equilibrium from which it will be possible to arrive at a solution of our problem by simple processes. We choose as our parameter the central density  $\rho_0$  of the convective core and show how it may sometimes be possible to find the suitable convective core to fit a given radiative envelope. It will be seen that a severe restriction on the mass within the core is necessary in order that a correct fit may be obtained. From the integral curves we have given it will be possible, firstly, to say if an adiabatic core suitable for the envelope really exists, and secondly, if it exists, how to find it simply. The luminosity condition, from this point of view, should be regarded as an independent one and is to be checked after a correct fit has been obtained. It is hoped that our curves will greatly facilitate the fitting of solutions.

#### THE METHOD OF SOLUTION.

The equations of equilibrium of a convective region are

$$\frac{dP}{P} = \Gamma_1 \frac{d\rho}{\rho} \quad (1)$$

where  $\Gamma_1$  is the adiabatic exponent and has the well-known value

$$\Gamma_1 = \beta + \frac{(4-3\beta)^2(\gamma-1)}{\beta+12(\gamma-1)(1-\beta)} \quad (1a)$$

$\beta = p_g/P$  = gas pressure/total pressure

$\gamma$  = ratio of the two specific heats

$$P = \frac{k}{\mu H} \rho T + \frac{1}{3} a T^4 \quad (2)$$

$$\frac{dP}{dr} = -G \frac{M(r)}{r^2} \rho \quad (3)$$

$$\frac{dM(r)}{dr} = 4\pi r^2 \rho \quad (4)$$

The constants  $k$ ,  $H$ ,  $a$ ,  $G$  have their usual meanings and  $\mu$  = mol. wt. We shall assume an abundance of hydrogen in the stellar matter of which there is ample evidence

and put  $\mu = 1$  throughout. These are also the equations used by Biermann. We briefly describe below how they are to be treated from the point of view of the parameter we are using.

Equation (1) when integrated with the aid of (1a) and (2) will furnish us series of  $(P, \rho)$  values on solutions corresponding to different initial values. We construct a series of solutions from the centre of the configuration *with a fixed  $P_0$  and continuously varying  $\rho_0$* , these being the values at the centre are, in fact, arbitrarily chosen. Putting  $\log \rho = x$ ,  $\log P = y$  equation (1) may be written in the form

$$\frac{dy}{dx} = \Gamma_1 \quad \dots \quad (1b)$$

which lends itself easily to integration. For assigned  $P$  and  $\rho$ , equation (2) gives  $T$  and hence  $\beta$  which we require for the computation of the function  $\Gamma_1$  at every stage. The ratio of the sp heats occurring in the expression for  $\Gamma_1$  is taken to be  $5/3$ , as for a monatomic gas. Starting successively with the initial values  $x = 2, 2.5, 3, 3.5, 4, 4.25, 4.5$  and  $y = 36.1281$  for all cases, we obtain sets of  $(P, \rho)$  solutions. The solutions all correspond to the same central pressure ( $P_0 = 4.9 \times 10^{15}$ ) but different central densities. It can be shown that from such a set of solutions it is possible to obtain by suitable transformations, solutions for different sets of central  $(P, \rho)$  values. Starting next with the same set of central values for  $P$  and  $\rho$  as above and with  $M(r) = 0$  at  $r = 0$ , we proceed to integrate equations (3) and (4). For this purpose we transform the equations to more convenient forms to express the variables in terms of solar units by the following substitutions

$$\begin{aligned} P &= P_0 p \\ M(r) &= M_0 m \\ r &= r_0 x \end{aligned} \quad (5)$$

where  $P_0 = 4.9 \times 10^{15}$ , fixed central pressure

$$M_0 = 2 \cdot 10^{33} \text{ (solar mass)}$$

$$r_0 = 7 \cdot 10^{10} \text{ (solar radius)}$$

and obtain the equivalent set as

$$\frac{dp}{dx} = -\beta \frac{m}{x^2} p$$

$$\frac{dm}{dx} = \alpha p x^2$$

$$\text{with} \quad \alpha = 4\pi r_0^3 / M_0, \quad \beta = GM_0 / r_0 P_0 \quad (6)$$

The method of integration is exactly the same as that reported in a previous communication (Burman, 1942). Thus we imagine that for a given central pressure, and continuously varying central density as a parameter, a series of one parametric solutions is obtained. Corresponding to every solution we form a table (shown in the appendix) of values for  $r, \rho, P, M(r), \log(r^3 \rho), \log(r^4 P)$  and plot the functions  $\log(r^4 P), \log(r^3 \rho)$  as in Fig. 1, the value of  $\rho_0$  attached to a curve showing with what central density the curve is associated in our integration.

We now show how this single set of curves enables us to construct all solutions corresponding to arbitrary central  $(P, \rho)$ -values. To see this we note that the equations (1)-(4) are invariant under the following transformations

$$\begin{aligned} \bar{\mu} &= \mu \\ \bar{P} &= \xi^4 P \\ \bar{\rho} &= \xi^3 \rho \\ \bar{T} &= \xi T \\ \bar{r} &= \xi^{-1} r \\ \bar{M}(r) &= M(r) \quad \dots \quad \dots \quad \dots \quad \dots \quad (7) \end{aligned}$$

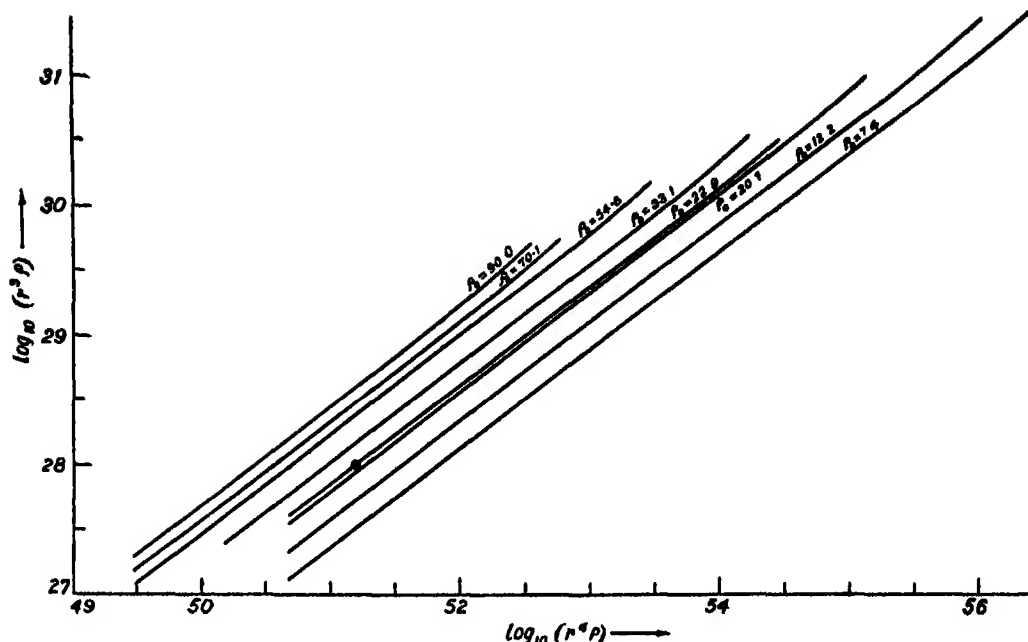


FIG 1

The curve  $\rho_0 = 22.9$  is a particular case where we determined the density parameter through a given point indicated in the figure

and further  $\beta$ ,  $M(r)$ ,  $r^4 P$ ,  $r^3 \rho$  are all invariants for this transformation. To construct the solution corresponding to any arbitrary central  $(P, \rho)$ -values, say  $(P_0', \rho_0')$ , we have to proceed as follows. We determine the transformation factor  $\xi$  from the relation  $P_0' = \xi^4 P_0$  and find out the density  $\rho_0$  (say)  $= \rho_0' / \xi^3$ . From the single infinity of solutions supposed to have been constructed with a fixed central pressure  $P_0$  and continuously varying central densities, we pick out that one which corresponds to the central value  $\rho_0$  of the density, and this solution subjected to the transformations (7) will furnish us the desired solution. It is thus seen that the set of solutions we already have at our disposal represents the totality of all solutions of the equations (1)–(4).

We shall make use of the invariance property of  $r^4 P$ ,  $r^3 \rho$  in continuing the solution through the convective core from the inner boundary of the radiative envelope. Suppose  $P', \rho', M(r')$  are the prescribed values of the pressure, density, and mass at a given distance  $r'$  (corresponding to the inner boundary of the radiative envelope). We have to find, if possible, a solution of the equations (1)–(4) which, in addition to satisfying the central conditions, will have these given values  $P', \rho', M(r')$  at  $r = r'$ .

In practice seven integrations have been performed for  $P_0 = 4.9 \times 10^{16}$  and  $\rho_0 = 7.39, 12.18, 20.1, 33.1, 54.6, 70.1, 90.0$  respectively. In Fig. 1, we have plotted curves between  $\log(r^4 P)$  and  $\log(r^3 \rho)$  corresponding to these solutions. To find a fit for the given solution  $P', \rho', M(r')$  at  $r = r'$  we plot in Fig. 1 the point  $\odot$ , whose co-ordinates are  $\log(r^4 P')$  and  $\log(r^3 \rho')$  and determine the parameter,  $\rho_0(\odot)$  (say), for that member of the family of curves which passes through this point  $\odot$ . An accurate determination of this parameter is a matter of some difficulty and we shall discuss it below at some length. Knowing  $\rho_0(\odot)$  we construct a solution of the equations (1)–(4) with initial values  $P_0, \rho_0(\odot)$  and obtain the curve passing through the point  $\odot$ . All solutions derived from this particular solution by the transformations (7) are also represented by the same curve. A reference to our table for the solution  $P_0, \rho_0(\odot)$ , gives the values of the variables at the point  $\odot$  as  $r, \rho, P$  and  $M(r)$ , say. We can now find the transformation factor  $\xi$  such that  $\xi^{-1} r = r'$ , and then  $P' = \xi^4 P, \rho' = \xi^3 \rho$  are automatically satisfied, since

$$r'^4 P' = r^4 P = (r\xi^{-1})^4 (\xi^4 P) = r'^4 (\xi^4 P)$$

$$r'^3 \rho' = r^3 \rho = (r\xi^{-1})^3 (\xi^3 \rho) = r'^3 (\xi^3 \rho)$$

But  $M(r)$  is an invariant of the transformation and if the fit is to be perfect  $M(r)$  should coincide with the given  $M(r')$ . Unless this happens it is not possible to compress the given mass of matter  $M(r')$  into an adiabatic core of radius  $r'$  and to have the pressure and density equal to  $P'$  and  $\rho'$  at the surface  $r'$ . Thus a fit with the solution of a convective core is not possible with arbitrary values of  $r'$ ,  $\rho'$ ,  $P'$  and  $M(r')$ . In case of  $M(r)$  and  $M(r')$  agreeing our method will determine the adiabatic core which will fit in with the given external solution.

After a fit has thus been obtained the suitability of the model will depend on whether the luminosity calculated by the energy generation formula agrees with the luminosity  $L(r')$  at  $r = r'$ .

#### DETERMINATION OF $\rho_0$ ( $\odot$ )

This problem may be stated thus—Given certain members of a family of one parametric curves on a plane, to find the parameter associated with that member of the family which passes through an assigned point. The solution here has been effected by a numerical method as the following. We draw an ordinate through the given point intersecting the family of curves, each curve at one point. The parameter for each of these points is given and from these by interpolation we obtain a value of the desired parameter. We might as well adopt the same procedure by drawing an abscissa through the given point, but, in the case under consideration, as it appears that the curves are more closely packed along an ordinate than along an abscissa, the first procedure furnishes smaller intervals for the argument and is, therefore, expected to give a more accurate result. An obvious improvement will be to obtain a large number of members of the family of curves more or less equi-spaced and thereby make the intervals of interpolation as small as possible. However, a particular case ( $\rho_0 = 22.9$ ), which we have worked out by this method, proved to be very satisfactory. With the value of the parameter thus obtained it will be necessary to construct a solution of the equations (1)–(4) with initial values  $P_0$ ,  $\rho_0(\odot)$  and draw the corresponding  $(r^4 P, r^3 \rho)$ -curve. If this curve does not happen to pass through the given point, a better value can be obtained by the method of trial and error.

#### SUMMARY

Curves have been given in Fig. 1 with the help of which the problem of fitting a convective core to a radiative envelope in stellar models, when this is feasible, can be solved. The mass of the core cannot be arbitrarily chosen and is in fact uniquely determined by the density and pressure on the surface of the core. Unlike the method described by Blanch, Lowan, Marshak and Bethe (1941), our present method takes into account the influence of radiation pressure and will be applicable in the case of massive stars. Tables of numerical integration are given in the Appendix for future reference.

The author takes this opportunity of acknowledging his gratefulness to Prof. N. R. Sen for his interest in this work and helpful discussions.

#### Note added in proof—

Since this paper was sent to the press, it has come to the notice of the author, that in a recent issue of the *Astrophysical Journal* (Vol. 96, p. 106, 1942), Henrich has completed some stellar models with a convective core fitted on to a radiative envelope by a method different from ours.

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## APPENDIX.

Solutions for different central densities ( $\rho_0 = 7.39, 12.18, 20.1, 33.1, 54.6, 70.1, 90.0$  gm/cm<sup>3</sup>) but same central pressure  $P_0 = 4.9 \times 10^{13}$  dynes/cm<sup>2</sup>

$\rho_0$	$x \cdot 10^3$	$\rho$	$p$	$m$	$\log_{10} (r^4 P)$	$\log_{10} (r^3 p)$
7.39	0	7.39	1	0		
	40	7.34	0.9879	$33.9 \times 10^{-5}$	53.4737	29.2173
	80	7.18	9524	$26.8 \times 10^{-4}$	54.6618	30.1007
	120	6.92	8820	88.2	55.3395	30.6130
	160	6.55	8218	$20.3 \times 10^{-3}$	55.8018	30.9638
	200	6.12	7358	37.9	56.1414	31.2251
	240	5.66	6425	62.6	56.3993	31.4287
	280	5.12	5469	94.0	56.5973	31.5862
	320	4.53	4537	$13.1 \times 10^{-2}$	56.7482	31.7070
	360	4.02	3601	17.4	56.8594	31.8084
	400	3.50	2865	22.1	56.9361	31.8857
12.18	0	12.18	1	0		
	20	12.15	0.9917	$69.8 \times 10^{-5}$	52.2710	28.5229
	40	11.98	9672	$55.9 \times 10^{-4}$	53.4641	29.4198
	60	11.68	9274	$18.5 \times 10^{-3}$	54.1507	29.9373
	80	11.30	8744	42.9	54.6247	30.2977
	100	10.80	8105	81.6	54.9794	30.5687
	140	9.54	6616	$20.8 \times 10^{-2}$	55.4756	30.9531
	180	7.98	5043	40.1	55.7945	31.2032
	220	6.52	3622	65.1	55.9901	31.3767
	282	6.10	3224	73.4	56.0410	31.4171
20.1	0	20.1	1	0		
	16	19.7	0.9859	$58.6 \times 10^{-5}$	51.8808	28.4421
	32	19.3	9449	$46.0 \times 10^{-4}$	53.0668	29.3365
	48	18.5	8795	$15.2 \times 10^{-3}$	53.7396	29.8461
	64	17.6	7949	34.8	54.1957	30.1994
	80	16.3	6956	65.3	54.5254	30.4568
	96	14.6	5911	$10.7 \times 10^{-2}$	54.7715	30.6466
	112	13.0	4871	15.8	54.9550	30.7968
	128	11.4	3886	21.9	55.0889	30.9138
	140	10.1	3206	26.9	55.1610	30.9779
33.1	0	33.1	1	0		
	12	32.8	0.9780	$40.9 \times 10^{-5}$	51.3777	28.2888
	24	31.4	9148	$31.9 \times 10^{-4}$	52.5527	29.1728
	36	29.6	8174	$10.4 \times 10^{-3}$	53.2082	29.6755
	48	26.7	6972	23.3	53.6388	30.0054
	60	23.6	5680	42.3	53.9377	30.2428
	72	20.3	4406	67.0	54.1438	30.4147
	84	17.5	3236	96.7	54.2778	30.5512
54.6	0	54.6	1	0		
	8	54.0	0.9733	$20.0 \times 10^{-5}$	50.6712	27.9770
	16	51.8	8969	$15.7 \times 10^{-4}$	51.8397	28.8619
	24	47.5	7801	50.4	52.4836	29.3526
	32	42.0	6425	$11.2 \times 10^{-3}$	52.8989	29.6741
	40	36.0	5001	20.0	53.1780	29.8979
	48	30.2	3691	30.9	53.3624	30.0589
	56	24.4	2539	43.7	53.4662	30.1673

Here  $x$  = radial distance in solar unit,  $\rho$  = density,  $p$  = (pressure at distance  $r$ )/(pressure at the centre), and  $m$  = mass in solar unit. The integrations are actually effected in quite a large number of steps of which we insert only a few.

$\rho_0$	$x 10^4$	$\rho$	$p$	$m$	$\log_{10} (r^4 P)$	$\log_{10} (r^3 \rho)$
70 1	0	70 1	1	0		
	44	69 5	0 9868	$42.8 \times 10^{-7}$	49 6388	27 3078
	84	67 8	9529	$29.2 \times 10^{-8}$	50 7468	28 1394
	124	65 5	9005	92 0	51 3987	28 6317
	164	62 4	8325	$20.7 \times 10^{-8}$	51 8502	28 9749
	204	59 0	7526	38 4	52 1856	29 2350
	244	55 0	6646	63 1	52 4428	29 4379
	284	50 8	5725	94 9	52 6416	29 6011
	324	45 6	4802	$13.4 \times 10^{-4}$	52 7940	29 7258
	332	44 4	4623	14 2	52 8199	29 7460
90 0	0	90 0	1	0		
	40	89 0	0 9819	$41.3 \times 10^{-7}$	49 4711	27 2910
	80	86 3	9299	$32.2 \times 10^{-8}$	50 6514	28 1806
	120	81 6	8491	$10.5 \times 10^{-8}$	51 3164	28 6846
	160	75 2	7474	23 8	51 7606	29 0238
	200	68 4	6337	44 0	52 0765	29 2734
	240	60 6	5163	71 0	52 3043	29 4584
	280	52 0	4041	$10.4 \times 10^{-4}$	52 4659	29 5929
	320	44 2	3028	14 1	52 5726	29 6963



## ON THE ARROW-WORMS OF KRUSADAI<sup>1</sup>

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(Communicated by Rai Bahadur Dr S L Hora, D Sc, F R S E, F N I)

(Received September 5, 1942)

The three genera of Chaetognatha, viz, *Sagitta* (Slabber), *Spadella* (Langerhans), and *Krohnia*<sup>2</sup> (Langerhans), are well represented in the Krusadai plankton. The importance of these arrow-worms, as indicators of water movement in the sea, has recently been emphasized by Kemp (1938). In this paper an attempt is made to give a brief account of the Krusadai forms, with special reference to two genera which are new records for the area. For the purpose of this paper, altogether 273 hauls of plankton from 2 to 15 fathoms were collected from the seas around the Krusadai Island, and examined at the Krusadai Biological Station during the years 1939, 1940 and 1941. The collections were made during both day and night.

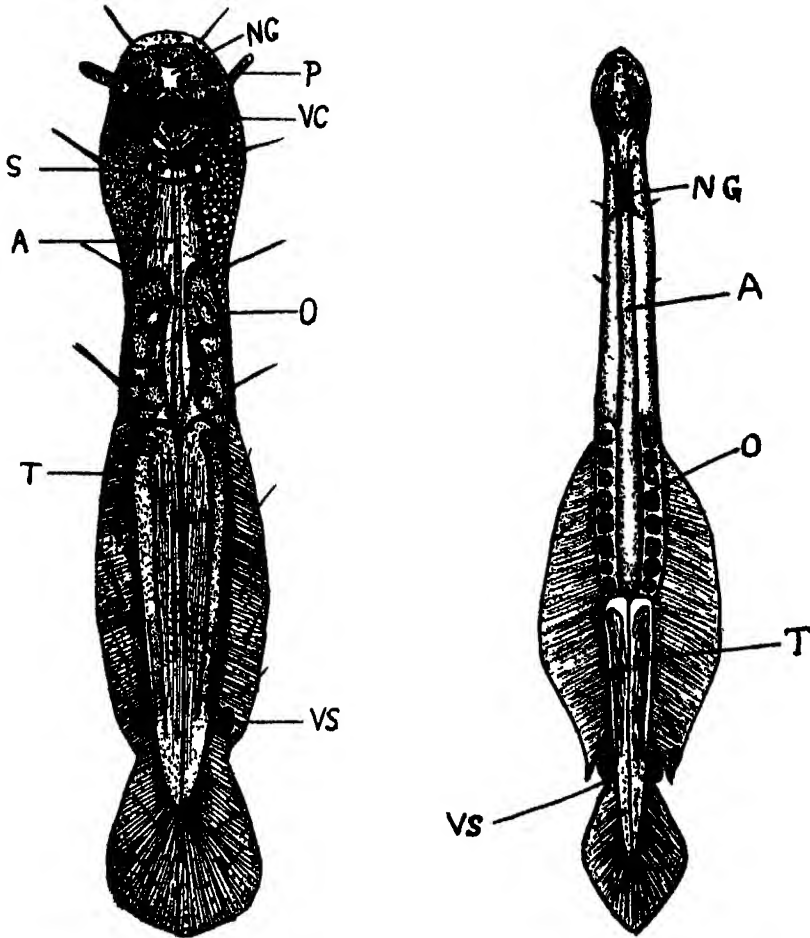
The commonest arrow-worms in the Krusadai plankton belong to the genus *Sagitta*. In Krusadai, *Sagitta robusta* (Doncaster) attains a maximum length of 18 mm whereas Dr John has recorded a maximum length of 11 mm for this arrow worm at Madras. *Sagitta enflata* (Grassi), *Sagitta tenuis* (Conant), *Sagitta robusta* (Doncaster), and *Sagitta neglecta* (Aida) occur in the seas around Krusadai throughout the year. Of these *S enflata* and *S tenuis* occur in abundance.

*Spadella cephaloptera* (W. Busch), from the Krusadai plankton, is easily distinguished by its single pair of lateral fins extending all round the tail. The body is transparent. The length varies from 2.7 to 3 mm. On the head there are 6 to 8 prehensile spines, 5 to 9 teeth and a pair of lateral tentacles near the base of the prehensile spines. The corona ciliata is oval and ring-shaped, and placed on the dorsal side of the neck. There is a remarkable parenchymatous tissue round the neck. There are groups of ciliated cells on the body forming wart-like projections. The ovary contains 3 to 5 large eggs, and the external opening of the ovary is surrounded by a conspicuous cement gland. The same arrow-worm recorded from the English Channel and the Mediterranean Sea is larger in size, being 4 to 5 mm long, the head carries 8 to 9 prehensile spines and 5 to 7 teeth. There are 6 to 8 large eggs in the ovary. The comparative smallness of the Indian specimens may be due to the tropical conditions under which they live. This kind of difference in size is noticed in the geographical distribution of many arrow-worms. Dr C C John, to whom specimens were sent for remarks, observes that the very few minor differences noticed between the *Spadellas* of Krusadai and those of the temperate regions do not appear to justify the creation of a new species for the Krusadai form. Nevertheless, this is the first time that *Spadella cephaloptera* (W. Busch) has been correctly recorded from the Indian waters. The only other species so far recorded from the Indian waters is *Spadella draco* by Doncaster (1903) from the Maldives and Laccadive Islands and by Dr. C C John from the Travancore Coast.

The Krusadai species of the genus *Krohnia* resembles *Krohnia pacifica* (Aida) in the following respects: (i) prehensile spines 7 to 8, (ii) teeth 10 to 12, (iii) lateral fins meet vesiculae-seminales, (iv) ova appear flattened, and (v) tail  $\frac{1}{2}$  of total length. The eyes are well distinguishable as a pair of small dark-blue spots, situated close together, 0.10 mm

<sup>1</sup> Published with the permission of the Director of Industries and Commerce, Madras.

<sup>2</sup> We are indebted to Dr. C C. John for confirming our identification of *Spadella* and *Krohnia*. We thank Dr. D. W. Devanessen for revising the manuscript.



× about 50

*Spadella cephaloptera* (W Busch) from Krusadai

× about 53

*Krohnia pacifica* (Aida)

A Alimentary canal, NG Nerve ganglion, O Ovary with eggs, P Papillae on head hood modified into club shaped tentacles, S Olfactory organ, T Testis, VC Commissure of ventral ganglion, VS Vesiculae seminales

apart As regards colour, the tip of the head has an orange tint and the body is greenish yellow, but these colours disappear in preserved specimens The lateral fin is broadest at the tail-septum, and the posterior ends of the lateral fins overlap vesiculae-seminales which are ovoid in shape and about 0.07 to 0.096 mm in thickness The tail fin also meets the vesiculae-seminales

#### BIONOMICS

The observation of 'double-headed monsters' of *Sagitta* mentioned by Shipley (1922) has been confirmed in the Krusadai Laboratory more than once. These arrow-worms have cannibalistic tendencies Shipley says (*op. cit.*, 190) that arrow-worms consume fish-eggs and fish-larvae But the food of the Krusadai arrow-worms consists mainly of copepods, we have not met with fish-eggs and fish-larvae in their stomach-contents. Species of *Sagitta* form an item of food for certain fishes. For instance, Hardy (1924) and Lebour (1921) found *Sagitta* in large numbers in the stomach of the European herring

*Clupea harengus* Of the fishes, whose stomach-contents were examined at the Krusadai Biological Station, only two, viz *Sardinella gibbosa* (Cuv & Val) and *Dussumieria hasselini* (Bleeker), were found to feed on *Sagitta*, whereas among the fishes examined in the West Hill Biological Station, four were ascertained as arrow-worm eaters, viz the Mackerel *Rastrelliger kanagurta* Russel, the Oil Sardine *Sardinella longiceps* (Cuv & Val), two Gogglers *Atule crumenophthalmus* (Bl) and *Decapterus kurra* (Cuv & Val)

Just as in the English Channel, in the San Diego Region, in the Atlantic Ocean and in other regions, the different species of Krusadai are found living together Topographical isolation or bathymetrical distribution or social isolation does not apparently exist

### DISCUSSION

It is noteworthy that there is a common social life among the several species of *Sagitta* of Krusadai The dominant species in this mixed community is *S. enflata* (Grassi), 50% of the collections being constituted by this species, a factor noticeable also in the *Sagitta* population of the Maldiva and Laccadive regions Not only is there a common social life but also a similarity in the cycle of seasonal fluctuations as will be seen from the table below

Total for three years, 1939, 1940 and 1941		<i>S enflata</i>	<i>S tenuis</i>	<i>S robusta</i>	<i>S neglecta</i>
1	January to April	910	490	370	325
2	May to August	585	195	140	125
3	September to December	2,655	1,315	400	400

Starting from January to April when, in the mixed community, the four species of *Sagitta* occupy a mean level, they show a decrease roughly to nearly 50% from May to August In the succeeding four months, September to December there is, in all the four species an unexpectedly abrupt rise There is thus a cycle of three stages (1) a mean level, (2) a decrease and (3) a precipitous rise The ecological factors responsible for these phenomena remain to be ascertained As there is a decrease in the hot months followed by a precipitous rise in the cold months in all the four species, temperature may be thought of as the controlling factor But the sudden drop in the case of *S enflata* and *S tenuis* from January to April cannot be attributed to temperature alone, for the gradient in the fluctuation of the population of *S robusta* and *S neglecta* for the same period is normal There may be a difference in the types of food of the two groups of *Sagitta* with whose fluctuations in abundance or occurrence, their fluctuations may be correlated Variations in the salinity, phosphate contents and pH value of the sea-water may be other governing causes *Krohnia pacifica* is more common in the off-shore plankton than in the inshore plankton thereby indicating that this species finds the conditions in the open sea more congenial

Apart from the hydrographical conditions, the geographical position of the Krusadai Island, lying as it does in that part of the sea where the Palk Straits unite with the Gulf of Manaar constitutes an important factor The fauna and flora of these seas are the richest known in South India During the cold season, the direction of the current is from the Palk Bay to the Gulf of Manaar through the Palk Straits As the species of *Sagitta*, *Spadella* and *Krohnia* are common during this season, it can be presumed that these arrow-worms drift southwards with the current

### SUMMARY

Two species, *Spadella cephaloptera* (W Busch) and *Krohnia pacifica* (Aida) are new records for Krusadai This is the first time that *Spadella cephaloptera* (W Busch) is correctly recorded from the Indian waters The arrow-worms of Krusadai reach their maxima during the cold season when there is plenty of rainfall, and when the surface temperature, salinity, specific gravity and pH value of the sea-water are low The arrow-

worms possibly drift southwards from Palk Bay through the Palk Straits into the Gulf of Manaar

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# ON THE POSSIBILITY OF CULTURE OF CERTAIN MARINE MULLET IN FRESHWATER TANKS<sup>1</sup>

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(Communicated by Rai Bahadur Dr S L Hora, D Sc , F R S E , F N I )

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In the shallow creeks and tide-pools of the Krusadar and Pamban Islands, fry of three species of Mullet, namely, *Mugil troscheli*, *M waigiensis* and *M sehel* are found throughout the year. *Mugil troscheli* is, however, the dominant species. *Mugil sehel* is of small size and its fry is not found in abundance. With a view to stocking Mullet-fry in the freshwater tanks of the neighbouring districts of Ramnad, Madura and Tinnevely, experiments were conducted at the Krusadar Biological Station in 1942 to find out a suitable method of conditioning the fry before transplanting them into tanks.

Mullet-fry were netted by a hand-net and transferred into a large canoe containing sea-water. The sea-water was changed every morning, and its salinity was gradually lowered by adding freshwater, the volume of water in the canoe was, however, always kept at 48 gallons. By daily increasing the proportion of freshwater, the fry were gradually acclimatized to a completely freshwater medium. The boat was anchored in the sea at a depth of two fathoms and covered with plaited coconut leaves to provide shade for the fry. Casualty were removed every morning and preserved for study.

*Experiment I*—On 19-3-1942 at 6 a.m., 180 fry of *Mugil troscheli*, ranging in size from 22 to 67 mm, were captured and released alive into a canoe containing sea-water of salinity 32.12‰. At 9 a.m., the sea water was changed and a mixture of sea-water and freshwater of a salinity of 30.14‰ poured into the boat. The casualty in this salinity was 2%. On 20-3-1942 at 9 a.m., the water in the canoe was changed to a lower salinity of 23.82‰. The casualty in this medium was only 1%. On 21-3-42 the salinity was lowered to 18.50‰ and on 22-3-1942 to 13.35‰. There was no casualty on these two days. On 23-3-1942 the water in the canoe was completely changed to almost freshwater of a salinity of 3.24‰. There was no casualty in this medium also. The percentage of fry of *Mugil troscheli* which survived the experiment was 97.

*Experiment II*—On 25-3-1942, 174 fry of *Mugil troscheli* and 22 of *M waigiensis*, ranging in size from 23 to 61 mm and from 29 to 51 mm respectively, were captured and released into the canoe containing sea-water of salinity 33.39‰, and the casualty in this was only 0.6% for *Mugil troscheli*. On 26-3-1942, the salinity was lowered to 15.70‰, the casualty in this was nil. On 27-3-1942 the water was completely changed to freshwater, the salinity being 1.00‰, and the casualty in this was only 0.6% for *Mugil troscheli* and 1% for *M waigiensis*. The percentages of fry that survived the experiment were: *Mugil troscheli* 98.8 and *M waigiensis* 99.

*Experiment III*—On 6-4-1942, 120 fry of *Mugil troscheli*, 22 to 62 mm in size, and 26 fry of *M waigiensis*, 33 to 52 mm in size, were captured and released in a canoe containing sea-water of salinity 33.75‰. The salinity was lowered to 20.03‰, the casualty in this medium was 1.5% for *Mugil troscheli* and 1% for *M waigiensis*. On 7-4-1942, the water in the canoe was completely changed to freshwater of salinity 1.84‰, this salinity was maintained for four days. The casualty of *Mugil troscheli* on 7-4-1942 was 5% and on 8-4-1942, 1.5%, and for *M waigiensis* 1% on 9-4-1942. There was no casualty on 10-4-1942. The percentages of fry that survived this experiment were 92 for *M. troscheli* and 98 for *M waigiensis*.

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*Experiment IV*—On 22-6-1942, 303 fry of *Mugil troscheli*, ranging in size from 29 to 58 mm, were captured from the sea (salinity 36.09‰, and transferred into a canoe containing brackish water of salinity 10.46‰. The casualty in this salinity was 10%. On 23-6-1942, 24-6-1942 and 25-6-1942 the water was changed, and the salinity was 4.15‰, 0.60‰ and 0.60‰ respectively, and the casualty of these three days was 22%, 8% and 12% respectively. The percentage of fry that survived this violent experiment was 48.

It will be observed that the casualty in the fourth experiment was heavier than in the other three experiments owing to the greater range in the change of salinity. Previous conditioning of the Mullet-fry in sea-water of decreasing salinity as indicated in the second and third experiments is, therefore, necessary before transplantation.

*Mugil troscheli* is the commonest species found in large numbers and hence this species seems to be the best suited for transplantation in freshwater ponds and tanks of the neighbourhood. Capacity of acclimatization, rapidity of growth, non-cannibalistic habit and the availability of the fry in large numbers indicate that this marine mullet is a good Indian sea-fish for cultivation in freshwaters.

[Mulletts are shoal fishes of considerable economic importance and occur in all tropical and temperate regions. They are found in seas, estuaries and freshwaters, and certain species, even under natural conditions, are capable of tolerating great variations in salinity. Of the three species referred to by the authors in the above note, *Mugil troscheli* and *M. wuigiensis* are found in the seas, estuaries and freshwaters, while the last species is generally found in fresh and brackish waters (Weber, M. & de Beaufort, L. F., *Fish Indo-Austral Archipel*, 4, pp 244, 248, 252, 1922). In India, especially in Bengal, several species of Mulletts are cultured in fresh and brackish waters. For instance, *M. coracula* is cultured in ponds in the southern parts of Bengal (Hamilton, F., *Gangetic Fishes*, p 221, 1822, Hora, S. L., *Journ. Bombay Nat. Hist. Soc.*, 40, p 62, 1938), it is common in most rivers of the Gangetic system. This species is known to breed in tanks and for this reason De (De, K. C., *A Few Hints on Culture of Fish in Tanks in Eastern Bengal and Assam*, p 3, Calcutta, 1936) has recommended that tanks need only be stocked with this fish once after which they will only require 'periodic thinnings and no replenishing'. The other Indian freshwater species of Mulletts are *M. cascasi* and *M. hamiltoni*. In the estuaries of the Ganges, *M. tade* and *M. parsia* are extensively cultured in the salt-water embanked fisheries known as 'Bhasa-badha'. Further, it is known in these parts that Mulletts grow to a big size only if allowed to enter into freshwaters, especially in the second year of their growth and, therefore, facilities are generally provided for them to migrate into paddy fields or adjoining freshwater canals. In the estuaries, however, the change in salinity is more or less gradual and, therefore, the fry of Mulletts get conditioned under natural conditions for life in freshwaters. Devanesean and Chacko have, however, shown how fry obtained from the sea can be conditioned under artificial conditions for planting in freshwater tanks and the method recommended by them is of great practical importance for the culture of fishes in areas adjoining the sea-shore. It must be remembered that during the breeding period of Mulletts (February to April in Bengal), the waters are simply thick with their fry so that only a little trouble has to be taken in collecting and planting the fry into suitable pieces of water.

In the *Statesman* of the 23rd April, 1942, it was reported that the Department of Fisheries of Egypt 'transferred millions of small fish from the sea to the lakes' with the result that Egypt's fish-supply, which had decreased to 12,000 tons increased to 40,000 tons a year. This increased supply of fish is stated to have solved the meat shortage problem of the country. It seems probable that the small marine fish of Egypt transferred to lakes were the young of Mulletts.—S. L. Hora, *Editor*]

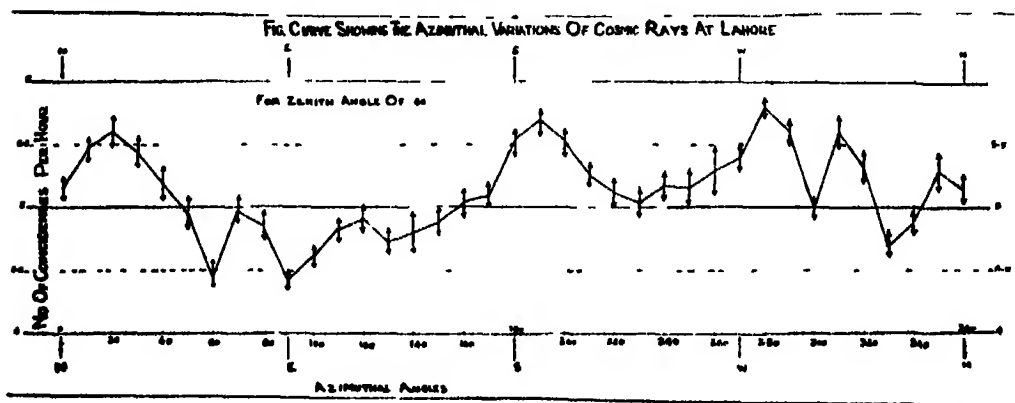
# THE AZIMUTHAL EFFECT OF COSMIC RAYS AT LAHORE

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(Communicated by Prof M N Saha, D Sc , F R S , F N I )

(Received April 8, 1943 )

The 'Azimuthal Effect' is the variation of cosmic-ray intensity at a fixed zenith angle and for different azimuths. Lemaitre and Vallarta (1936) considered the azimuthal effect without taking into account the influence of the penumbra (Shremp, 1938). Historically the first case of the azimuthal effect was discovered by Rossi (1930), who determined the east-west asymmetry in cosmic radiation both experimentally and theoretically. Experiments of Rossi were followed by those of Johnson (1934), Alvarez and Compton (1933) and others. Most of all these experiments explored the east-west and north-south planes and neglected other azimuths.



The theory of the effect of the earth's magnetic field on cosmic rays has been worked out by Lemaitre and Vallarta and their collaborators. The cone, in which the charged particles of a given energy may arrive at a given point of the earth from all directions, is known as the allowed cone. It consists of the 'main cone' within which all directions are allowed and the 'shadow cone' outside of which all directions are forbidden. The 'penumbra' is the region between the above two cones within which certain bands of directions are allowed and the rest forbidden. The penumbra is important at intermediate latitudes (between  $10^\circ$  and  $40^\circ$  geomagnetic).

R. Albagh Hutner (1939) has determined the azimuthal effect at  $20^\circ$  geomagnetic latitude taking into account the penumbra, whose banded structure gives humps in the cone showing the azimuthal effect. In the present paper are discussed the results on the azimuthal variation of cosmic radiation at Lahore (geomagnetic latitude  $22^\circ\text{N}$ ).

## THE EXPERIMENTAL ARRANGEMENT

In measuring the intensity (number of coincidences from that direction per unit time) of cosmic rays, four cosmic-ray telescopes were used, each consisting of three triple coincidence G-M counter tubes with lead filter of 10.2 cm. The solid angle range covered by each telescope was  $8.07^\circ$  in the vertical and  $38.87^\circ$  in the lateral planes. The telescopes were mounted on four edges of a square table, which was rotated back and forth through

an angle of  $180^\circ$ , so that opposite telescopes interchanged positions at regular intervals. The interchanging of the opposite telescopes make it possible to compare the cosmic-ray intensities from opposite directions. The azimuths were changed by steps of  $10^\circ$  each time. Each of the four telescopes covered the horizon for the fixed zenith angle at intervals of  $10^\circ$  at least twice. The G-M tubes were tested frequently to assure their consistent working.

The apparatus was installed in a special observatory constructed for the purpose, on top of the physics laboratory of Forman Christian College, Lahore. The roof of the observatory was made of a single sheet of galvanized iron and was thus virtually open to the sky.

Each point of the given curve represents the mean of the data collected by all the four telescopes. The data were collected between October 31, 1941 and February 21, 1942. A glance at the curve clearly shows the marked irregularities in the north-west quadrant, while no such marked variations are shown in the other quadrants. Two humps, one at  $280^\circ$  and the other at  $310^\circ$  are prominent in the north-west quadrant. The curve in the north-east quadrant varies considerably less. This is in agreement with Hutner's conclusion that in the northern hemisphere, the curve between the north and east directions should be less irregular because of the supposed predominance of positive particles.

Hutner's results refer strictly to primaries before they enter the atmosphere. In the present experiment the secondaries were filtered off by 10.2 cm of lead and therefore telescopes recorded the passage of hard secondaries presumably having the same direction as the primaries which were responsible in producing them.

Special cases of the 'Azimuthal Effect' are the east-west and north-south asymmetries. These asymmetries can be calculated from the given curve. Bhattacharya (1942) observed the east-west asymmetry of the penetrating component of cosmic rays at Calcutta (geomagnetic latitude  $12^\circ\text{N}$ ) for various zenith angles. His value for zenith angle  $60^\circ$  is  $0.62 \pm 5.98$  per cent, the intensity being of course, greater from the west. The value for the east-west difference from the above curve is found to be  $19.5 \pm 3.0$  per cent.

It is found that the maximum east-west difference does not coincide with the magnetic east-west plane, but is found to occur in the  $280^\circ$ - $100^\circ$  plane. This point is being further investigated in this laboratory and it is hoped that the results will be reported in the near future.

The author wishes to express his thanks to the University of the Punjab for granting a fellowship for continuing these experiments at Lahore, to the University of Chicago for supplying the apparatus, and to the Forman Christian College for the facilities of the Physics Department.

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## THE OVULE AND EMBRYO SAC OF *FOUQUIERIA*

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(Communicated by Dr P Maheshwari, D Sc, F A Sc, F N A Sc, F N I)

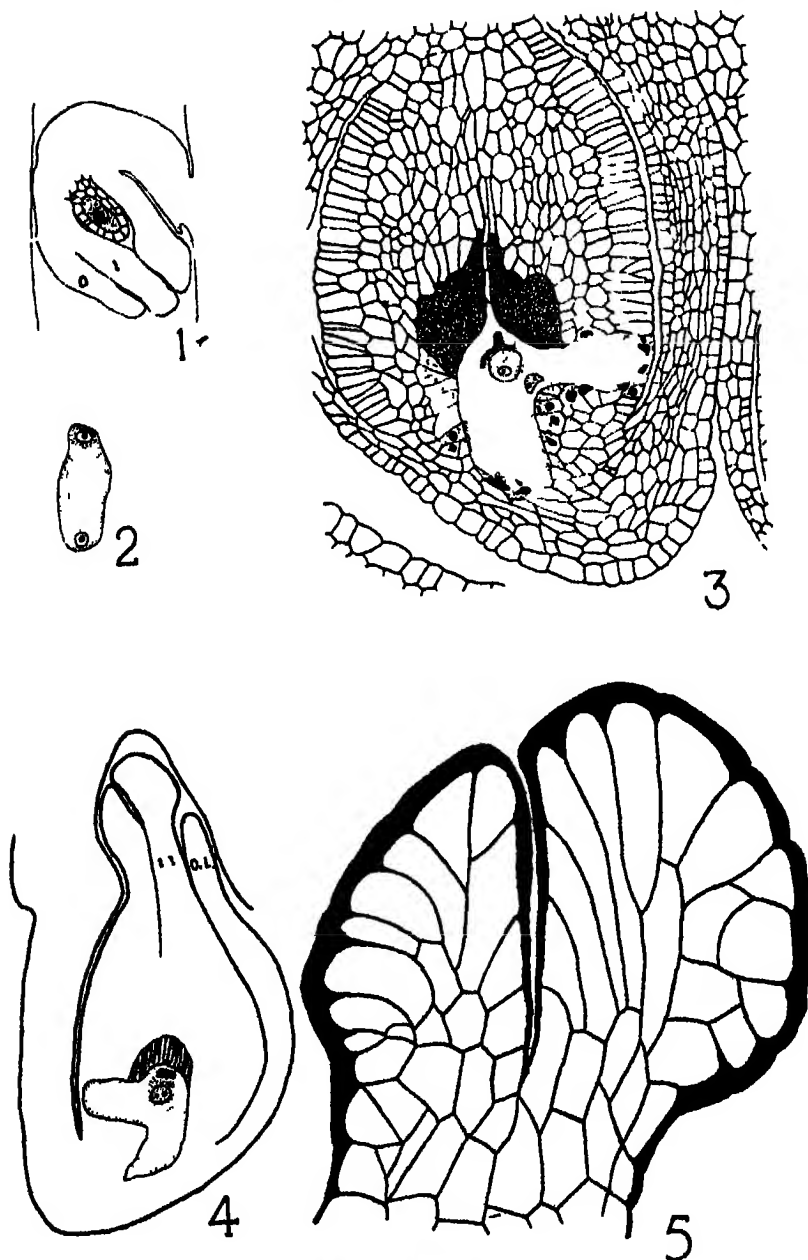
(Received February 23, 1943)

During the course of a personal discussion on the presence of a nucellar epistase in angiosperms, Dr P Maheshwari invited my attention to D A Johansen's (1936) paper on the 'Morphology and embryology of *Fouquieria*' and remarked that the author had evidently mistaken the inner integument for the nucellus. A further study of the paper revealed that the development of the embryo sac had also been wrongly described as tetrasporic. Mauritson (1936), who studied *Fouquieria splendens* independently and without any knowledge of Johansen's work, has shown that the nucellus is very meagre in the young ovule and, as the latter grows older, disappears completely, the embryo sac being then in direct contact with the inner integument. He also shows that the development of the embryo sac is of the Normal type.

Although Mauritson has given a correct account of *F. splendens*, a comment on Johansen's (1936) paper is felt necessary for various reasons.

Johansen (1936, p 95) writes 'Each ovule is invested with an inner and an outer integument (Fig 1). The inner integument precedes the outer in time of origin. The former furthermore grows faster and is thicker by reason of possessing a larger number of layers of cells. The elongated lips of the inner integument soon meet above the nucellus and there become considerably swollen, the nucellus is thus completely enclosed.' So far his account appears to be quite correct and agrees with his Fig 1 (reproduced here also as Fig 1). The nucellus clearly consists of only 1-2 layers of cells and the megaspore mother cell is situated directly below the epidermis. But there is a remarkable disagreement between this and what he writes later. On pp 95-96 he states 'In the nucellus, crowning the megagametophytic cavity, and apparently forming part of the tapetum, there is situated a group of thick walled vertically elongated cells (Fig 9). The walls of these cells become suberised during the maturation of the seed, and move upward toward the micropylar end of the ovule while the surrounding nucellar cells are being destroyed to make room for the cellular endosperm. The group apparently breaks through the epidermis of the nucellus at the apex of the latter and becomes plugged between the lips of the inner integument, blocking the opening through which the pollen tube entered.' These cells, in his opinion, constitute a kind of epistase. His Fig 9 (redrawn as Fig 3 here) shows a mature embryo sac surrounded by a thick tissue of cells which, according to him, is the nucellus and some of whose cells are said to form the epistase (shaded in Fig. 3). On one side of the supposed nucellus is the raphe and on the other a single integument. Since the figure shows no structure between this nucellus and the raphe, one is immediately led to ask 'Where is the inner integument and where are its thick lips which enclose the nucellus and become plugged by the epistase?' On that side also, which is away from the raphe, there is only one integument instead of two. The inevitable conclusion is that what Johansen has taken to be the nucellus is itself the well-developed and massive inner integument. It is strange that although Johansen earlier speaks of a well-developed inner integument, its absence in his Figures 8 and 9 did not strike him as something problematic.

A well-developed nucellus, projecting through the micropyle is not unknown in some other angiosperms. It is so in the Malpighiaceae for instance (Stenar, 1937; Subba Rao, 1940), but here there can be no confusion as both the integuments are present in addition to the nucellus.

FIGS 1-5 *Fouquieria*.

FIGS. 1-3 Redrawn from Johansen's Figs. 1, 2 and 9 respectively.

Fig. 1 *F. splendens* Median longitudinal section of young ovule showing the megasporocyte surrounded by the inner (i) and outer (o) integuments. Fig. 2 *F. splendens*. Binucleate megagametophyte  $\times 368$ . Fig. 3 '*F. burragii*. Median longitudinal section of ovule with mature pentanucleate megagametophyte. Notice the canal traversing the cap-like epistase (stippled). Redrawn from a photomicrograph'. Figs 4-5 *F. peninsularis*. Fig. 4 Longitudinal section of an ovule at the mature embryo sac stage, showing the outer (o) and inner (i) integuments. Note the thick 'lips' of the latter and the narrow micropyle (reconstructed from several sections).  $\times 120$ . Fig. 5 Apical portion of the inner integument magnified to show the micropyle.  $\times 608$ .

Fig 4, showing an ovule in longitudinal section, and Fig 5, showing a portion of the same on a more magnified scale, have been drawn from a preparation of *F. peninsularis* made by Johansen himself and presented to Dr Maheshwari. Here we find a narrow canal in the upper half of what Johansen supposes to be the nucellus. It is quite distinct and appreciably wide in the apical portion but narrows down towards the base fading out of sight near the middle. It obviously corresponds to the micropyle and, therefore, confirms the view that the supposed nucellus is the inner integument.

A probable cause of Johansen's misinterpretation is suggested by his Figs 1 and 2 (reproduced as Figs 1 and 2 respectively) and his account of the development of the embryo sac. He supposes that Fig 2 represents a stage immediately following that in Fig 1. Actually, however, he has missed, between these two, all the stages showing the division of the megaspore mother cell, the formation of the tetrad, and the growth of the functional megaspore. It seems clear that during this interval the nucellus is entirely used up by the growing megaspore, and the inner integument comes to lie in direct contact with the embryo sac.

It may also be added that if the nucellus has disappeared, the so-called 'epistase' must belong to the inner integument.

Coming to the development of the embryo sac, Johansen says that in *Fouquieria splendens*, *F. peninsularis*, and *F. burragei* it is tetrasporic. According to Mauritzon who investigated *F. splendens*, it is monosporic. Due to this difference in the reports of these authors, Maheshwari (1937) pointed out the need for a reinvestigation of these plants. After the megaspore mother cell stage, Mauritzon figures a row of three cells of which the uppermost is binucleate and the lowest much larger than others. The latter is obviously the functional megaspore formed as a result of the division of the megaspore mother cell. The embryo sac is consequently monosporic and there is no reason to doubt the validity of this conclusion. But there is also other evidence that goes to show that it is not tetrasporic as claimed by Johansen. As pointed out by Maheshwari (1941, p. 251), in the tetrasporic types a large central vacuole is usually not seen at the 2- and 4-nucleate stages but makes its appearance only when the four nuclei are preparing for the next division. Johansen's Fig 2 (Fig 2 here) shows this vacuole even at the 2-nucleate stage indicating that these nuclei do not represent the dyad stage but are the products of the first division of the megaspore nucleus. (See also Maheshwari, 1942, on *Euphorbia heterophylla*.)

Comparing *F. splendens* with *Myricaria germanica*, Johansen (p. 98) writes: '*F. splendens* and *M. germanica* follow an almost identical developmental scheme'. This comparison is entirely invalid not only because the embryo sac of *F. splendens* is monosporic but also because the development of the embryo sac in *Myricaria germanica* is not of the *Adoxa*-type as reported by Frisendahl (1912), on whose work Johansen bases his statement, but of the *Fritillaria*-type. As pointed out by Maheshwari (1937), Frisendahl's figures show the 1+3 arrangement of the nuclei at the four nucleate stage of the embryo sac as well as the difference in the relative sizes of the micropylar and chalazal pairs of nuclei of the 'four nucleate' stage—really the secondary four nucleate stage (see also Zabban, 1936, and Maheshwari, 1941).

Dealing with the haustorial function of the lateral arm of the mature embryo sac in *Fouquieria*, Johansen writes: 'Since there is no vascular supply in the funiculus or raphe, and there apparently exists no other method by which water and foodstuffs are transported to the ovule, the development of the haustorial arm may logically be considered the remedy of this defect'. The defect does not exist, however. The preparation of *F. peninsularis* presented by Johansen to Dr Maheshwari shows that the raphe does possess a vascular supply and the explanation for the occurrence of the haustorium must, therefore, be sought elsewhere.

#### SUMMARY

Johansen's observations on *Fouquieria* are criticised as the result of a careful study of his own figures and of a preparation of *Fouquieria peninsularis* presented by him to Dr. Maheshwari. It is concluded that:—

- 1 The nucellus in *Fouquieria* is not massive as claimed by Johansen but extremely reduced and all traces of it are lost during the development of the embryo sac
- 2 The ovule is provided with two integuments of which the inner is more massive and forms the micropyle The 'epistase' of Johansen does not belong to the nucellus but to the inner integument
- 3 The ovule has a normal vascular supply in the raphe
- 4 The development of the embryo sac is not tetrasporic but monosporic as reported by Mauritzon (1936)

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# THERMODYNAMICS OF A FERMI-DIRAC GAS OBEYING BORN'S MODIFIED QUANTUM STATISTICS

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1 In a series of recent papers, Born (1938, 1939, 1940) has developed his 'Theory of Reciprocity', which fixes an upper limit to the momentum possible for a particle. This theory does for the momentum co-ordinates what Einstein's theory does for positional co-ordinates.

The number of wave-functions  $a(\epsilon)d\epsilon$  for a particle enclosed in a volume  $V$  and having energy between  $\epsilon$  and  $\epsilon+d\epsilon$  is given by, taking account of the finiteness of the momentum space,

$$a(\epsilon)d\epsilon = \frac{4\pi g V}{c^3 h^3} \frac{(\epsilon^2 + 2\epsilon mc^2)^{\frac{1}{2}}(\epsilon + mc^2)d\epsilon}{\left(1 - \frac{\epsilon^2 + 2\epsilon mc^2}{b^2 c^2}\right)^{\frac{1}{2}}}, \quad (1)$$

where  $b$  is the radius of the closed momentum space,  $c$  is the velocity of light, and  $g$  the weight factor of the particle due to its internal structure. We shall use the above expression to calculate some of the well-known thermodynamic functions for an assembly consisting of similar and non-interacting particles obeying Fermi-Dirac statistics. In the usual treatment the momentum space is taken to be infinite ( $b \rightarrow \infty$ ), and it is of interest, therefore, to see to what extent the thermodynamic properties of an assembly get modified when the momentum space is restricted in the manner contemplated by Born. Born has already discussed the case of a classical gas and that of radiation. In the present paper we shall consider the degenerate and non-degenerate cases of a Fermi-Dirac gas on the basis of finite momentum space.

2 According to Fermi-Dirac distribution law the number of particles  $N(\epsilon)d\epsilon$  having energy between  $\epsilon$  and  $\epsilon+d\epsilon$  is given by

$$N(\epsilon)d\epsilon = \frac{4\pi g V}{c^3 h^3} \frac{(\epsilon^2 + 2\epsilon mc^2)^{\frac{1}{2}}(\epsilon + mc^2)d\epsilon}{\left(1 - \frac{\epsilon^2 + 2\epsilon mc^2}{b^2 c^2}\right)^{\frac{1}{2}} \left(1 + e^{\frac{\epsilon - \zeta}{kT}}\right)}, \quad (2)$$

where  $\frac{\zeta}{kT}$  is the discriminant for the degenerate and non-degenerate cases ( $\frac{\zeta}{kT} \gg 1$  corresponds to the degenerate case and  $\frac{\zeta}{kT} \ll 0$  corresponds to the non-degenerate case.)

Let  $N$  denote the total number of similar and non-interacting particles in an assembly at temperature  $T$ , and let  $E$  be the energy of the assembly, then,

$$N = \int_0^{\epsilon_1} N(\epsilon)d\epsilon, \quad (3)$$

and 
$$E = \int_0^{\epsilon_1} \epsilon N(\epsilon)d\epsilon, \quad (4)$$

where  $\epsilon_1$  is the energy corresponding to the momentum  $b$  and is given by the relation

$$\epsilon_1^2 + 2\epsilon_1 mc^2 = b^2 c^2 \quad (5)$$

The pressure ( $p$ ) of the assembly is, as usual, given by

$$p = \frac{4\pi g V}{3c^3 h^3} \int_0^{\epsilon_1} \frac{(\epsilon^2 + 2\epsilon mc^2)^{\frac{1}{2}} d\epsilon}{\left(1 - \frac{\epsilon^2 + 2\epsilon mc^2}{b^2 c^2}\right)^{\frac{1}{2}} \left(1 + e^{\frac{\epsilon - \zeta}{kT}}\right)} \quad (6)$$

If the assembly be considered to be reduced to absolute zero of temperature (its volume being unchanged), then the distribution law (2) gives

$$N(\epsilon) d\epsilon = \frac{4\pi g V}{c^3 h^3} \frac{(\epsilon^2 + 2\epsilon mc^2)^{\frac{1}{2}} (\epsilon + mc^2) d\epsilon}{\left(1 - \frac{\epsilon^2 + 2\epsilon mc^2}{b^2 c^2}\right)^{\frac{1}{2}}} \quad \text{for } \epsilon < \zeta_0$$

$$= 0, \quad \text{for } \epsilon > \zeta_0$$

where  $\zeta_0$  is the maximum energy of a particle in the completely degenerate case ( $T = 0$ ). It is defined by

$$N = \frac{4\pi g V}{c^3 h^3} \int_0^{\zeta_0} \frac{(\epsilon^2 + 2\epsilon mc^2)^{\frac{1}{2}} (\epsilon + mc^2) d\epsilon}{\left(1 - \frac{\epsilon^2 + 2\epsilon mc^2}{b^2 c^2}\right)^{\frac{1}{2}}} \quad (7)$$

$$= \frac{4\pi g V}{c^3 h^3} (\zeta_0^2 + 2\zeta_0 mc^2)^{\frac{1}{2}} \left\{ 1 + \frac{3(\zeta_0^2 + 2\zeta_0 mc^2)}{10b^2 c^2} + \frac{9(\zeta_0^2 + 2\zeta_0 mc^2)^2}{56b^4 c^4} + \dots \right\} \quad (8)$$

From (8) we have

$$m^3 c^6 x^3 = z^3 \left\{ 1 + \frac{3z}{10b^2 c^2} + \frac{9z^2}{56b^4 c^4} + \dots \right\}, \quad (9)$$

where  $z = \frac{N}{V}$ ,  $z = \zeta_0^2 + 2mc^2 \zeta_0$  and  $x = \frac{h}{mc} \left( \frac{3n}{4\pi g} \right)^{\frac{1}{3}}$ .

Inverting the series (9) we obtain

$$\zeta_0^2 + 2mc^2 \zeta_0 = m^3 c^4 x^3 - \frac{m^4 c^6 x^4}{5b^2 c^2} - \frac{3m^5 c^{10} x^6}{175b^4 c^4} \dots \quad (10)$$

$$\text{and} \quad \zeta_0 + mc^2 = mc^2 (1 + x^2)^{\frac{1}{2}} \left\{ 1 - \frac{m^2 c^4 x^4}{10(1 + x^2)b^2 c^2} - \frac{m^4 c^6 (12x^6 + 19x^8)}{1400(1 + x^2)^2 b^4 c^4} \right\} \quad (11)$$

In the completely relativistic case  $mc^2$  is negligible in comparison to  $\zeta_0$ , and  $x \rightarrow \infty$ ,

$$\zeta_0 = mc^2 x - \frac{m^3 c^6 x^3}{10b^2 c^2} - \frac{19m^5 c^{10} x^5}{1400b^4 c^4} \dots \quad (12)$$

and in the completely non-relativistic case  $x \rightarrow 0$

$$\zeta_0 = \frac{1}{2} mc^2 x^2 - \frac{m^3 c^6 x^4}{10b^2 c^2} - \frac{12m^5 c^{10} x^6}{1400b^4 c^4} \dots \quad (13)$$

Using \* (3) and (7) we have

$$\zeta = \zeta_0 - 2c_2 (kT)^2 \left\{ \frac{1}{\zeta_0 + mc^2} + \frac{\zeta_0 + mc^2}{\zeta_0^2 + 2mc^2 \zeta_0} + \frac{\zeta_0 + mc^2}{b^2 c^2} + \frac{(\zeta_0 + mc^2)(\zeta_0^2 + 2mc^2 \zeta_0)}{b^4 c^4} \right\} \quad (14)$$

\* The series expansion for the integrals occurring in the expressions for  $N$ ,  $E$  and  $p$  are given in the appendix

Expressing  $\zeta$  in terms of  $x$  by using (10) and (11) we get

$$\begin{aligned} \zeta = mc^2(1+x^2)^{\frac{1}{2}} - mc^2 - \frac{m^3c^6x}{10(1-x^2)^{\frac{1}{2}}b^2c^2} - \frac{m^5c^{10}(12x^6+19x^8)}{1400(1+x^2)^{\frac{1}{2}}b^4c^4} \\ - 2c_2(kT)^2 \left\{ \frac{1+2x^2}{mc^2x^2(1+x^2)^{\frac{1}{2}}} + \frac{mc^2(12x^4+23x^2+12)}{10(1+x^2)^{\frac{1}{2}}b^2c^2} \right. \\ \left. + \frac{m^3c^6(1326x^8+4085x^6+4260x^4+1480x^2)}{1400(1+x^2)^{\frac{1}{2}}b^4c^4} \right\} \end{aligned} \quad (15)$$

In the completely relativistic case  $x \rightarrow \infty$

$$\zeta = mc^2x - \frac{m^3c^6x^3}{10b^2c^2} - \frac{19m^5c^{10}x^5}{1400b^4c^4} - 2c_2(kT)^2 \left( \frac{2}{mc^2x} + \frac{6mc^2}{5b^2c^2} + \frac{1326m^3c^6x^3}{1400b^4c^4} \right) \quad (16)$$

In the completely non-relativistic case  $x \rightarrow 0$

$$\zeta = \frac{mc^2x^2}{2} - \frac{m^3c^6x^4}{10b^2c^2} - \frac{12m^5c^{10}x^6}{1400b^4c^4} - 2c_2(kT)^2 \left( \frac{1}{mc^2x^2} + \frac{6mc^2}{5b^2c^2} + \frac{37m^3c^6x^2}{35b^4c^4} \right) \quad (17)$$

We shall now determine the series expansion for energy. Using (4) and the result given in the appendix, we obtain in the completely relativistic case

$$E = \frac{\pi g V}{c^3 h^3} \left( \zeta_0^4 + \frac{\zeta_0^6}{3b^2c^2} + \frac{3\zeta_0^8}{16b^4c^4} + \dots \right) + \frac{4\pi g V}{c^3 h^3} 2c_2(kT)^2 \left( \zeta_0^2 + \frac{\zeta_0^4}{2b^2c^2} + \frac{3\zeta_0^6}{8b^4c^4} \right) \quad (18)$$

Substituting (12) in (18) we get energy in terms of concentration parameter  $x$

$$\begin{aligned} E = \frac{\pi g V}{c^3 h^3} \left( m^4c^8x^4 - \frac{m^6c^{12}x^6}{15b^2c^2} - \frac{19m^8c^{16}x^8}{2800b^4c^4} \right) \\ + \frac{4\pi g V}{c^3 h^3} 2c_2(kT)^2 \left( m^2c^4x^2 + \frac{3m^4c^6x^4}{10b^2c^2} + \frac{221m^6c^{12}x^6}{1400b^4c^4} \right) \end{aligned} \quad (19)$$

We obtain in the completely non-relativistic case

$$\begin{aligned} E = \frac{4\pi g V}{c^3 h^3} \left\{ \frac{1}{5} (2mc^2)^{\frac{1}{2}} \zeta_0^{\frac{5}{2}} \left( 1 + \frac{5mc^2\zeta_0}{7b^2c^2} + \frac{5m^2c^4\zeta_0^2}{8b^4c^4} \right) \right. \\ \left. + c_2(2mc^2)^{\frac{1}{2}}(kT)^2 \zeta_0^{\frac{3}{2}} \left( 1 + \frac{mc^2\zeta_0}{b^2c^2} + \frac{3m^2c^4\zeta_0^2}{2b^4c^4} \right) \right\} \end{aligned} \quad (20)$$

Expressing energy in terms of concentration we have

$$\begin{aligned} E = \frac{4\pi g V}{c^3 h^3} \left\{ \frac{1}{10mc^2} \left( m^5c^{10}x^5 - \frac{m^7c^{14}x^7}{7b^2c^2} - \frac{m^9c^{18}x^9}{105b^4c^4} \right) \right. \\ \left. + 2mc^2(kT)^2c_2 \left( mc^2x + \frac{2m^3c^6x^3}{5b^2c^2} + \frac{37m^5c^{10}x^5}{175b^4c^4} \right) \right\} \quad (21) \end{aligned}$$

The specific heat at constant volume is defined by

$$c_v = \left( \frac{\partial E}{\partial T} \right)_v$$

and can be easily obtained from (19) and (21). The expressions for the two cases of pressure can be obtained by integrating (8). We can, however, obtain them from

(19) and (21) by using the well-known results that  $p = \frac{1}{3} E$  in the completely relativistic

case and  $p = \frac{2}{3} E$  in the completely non-relativistic case

We proceed now to calculate the series expansion for the entropy  $S$ . We have the thermodynamic relation

$$TS = kT \int_0^{\epsilon_1} a(\epsilon) \log(1 + Ae^{-\epsilon/kT}) d\epsilon + E - N\zeta, \quad (22)$$

where  $a(\epsilon)$ ,  $E$  and  $N$  are given by (1), (4) and (3) respectively. Evaluating the integral and substituting the values, we get in the completely relativistic case

$$TS = 16c_2(kT)^2 \frac{\pi g V}{c^3 h^3} \left( \zeta^2 + \frac{\zeta^4}{2b^4 c^4} + \dots \right), \quad (23)$$

or in terms of concentration

$$TS = \frac{12c_2(kT)^2 N}{mc^2 x} \left( 1 + \frac{3m^2 c^4 x^2}{10b^2 c^2} + \dots \right) \quad (24)$$

In the completely non-relativistic case

$$TS = 16c_2(kT)^2 \frac{\pi g V}{c^3 h^3} (2mc^2)^{\frac{1}{2}} \zeta^{\frac{3}{2}} \left\{ 1 + \frac{mc^2 \zeta}{b^2 c^2} + \dots \right\} \quad (25)$$

Using (17) and (25) we have entropy in terms of concentration

$$TS = \frac{12c_2(kT)^2 N}{mc^2 x^2} \left( 1 + \frac{2m^2 c^4 x^2}{5b^2 c^2} + \dots \right) \quad (26)$$

Gibb's free energy  $G$  is defined by the relation

$$G = E + pV - TS \quad (27)$$

Substituting the values from (19) and (24), we have in the relativistic case

$$G = \frac{4\pi g V}{3c^3 h^3} \left( m^4 c^6 x^4 - \frac{m^6 c^{12} x^6}{15b^2 c^2} \right) - \frac{4c_2(kT)^2 N}{mc^2 x} \left( 1 + \frac{3m^2 c^4 x^2}{10b^2 c^2} \right), \quad (28)$$

and in the non-relativistic case we have

$$G = \frac{2\pi g V}{3c^3 h^3} \left( m^4 c^6 x^5 - \frac{m^6 c^{12} x^7}{7b^2 c^2} \right) - \frac{2c_2(kT)^2 N}{mc^2 x^2} \left( 1 + \frac{2m^2 c^4 x^2}{5b^2 c^2} \right) \quad (29)$$

It should be noted that in Born's modified quantum statistics  $G \neq N\zeta$ . In fact  $G - N\zeta =$  terms containing powers of  $\frac{1}{b}$  which vanish when  $b \rightarrow \infty$ .

3 We proceed to calculate the thermodynamic functions for the non-degenerate case  $\left( \frac{\zeta}{kT} \ll 0 \right)$ . In the completely relativistic case we have from (3)

$$N = \frac{4\pi g V}{c^3 h^3} \int_0^{\epsilon_1} \frac{\epsilon^2 d\epsilon}{(1 - \epsilon^2/b^2 c^2)^{\frac{1}{2}} \left( 1 + \frac{1}{A} e^{\epsilon/kT} \right)}, \quad \dots \quad (30)$$

where  $\epsilon_1 = bc$  and  $A = \exp \zeta/kT$

$$\text{Or} \quad N = \frac{4\pi g V}{h^3} b^3 \int_0^1 \frac{u^2}{(1-u^2)^{\frac{1}{2}}} \{ A e^{-\alpha u} - A^2 e^{-2\alpha u} + \dots \} du, \quad (31)$$

where  $\epsilon = bcu$ , and  $\alpha = \frac{bc}{kT}$ .

But 
$$\int_0^1 \frac{t^2 e^{-xt} dt}{(1-t^2)^{\frac{1}{2}}} = \frac{2}{x^3} + \frac{12}{x^5} + \frac{270}{x^7} + \dots, \quad (32)$$

if  $x \rightarrow \infty$

Therefore when  $\alpha \gg 1$ , (31) gives

$$A_0 = \frac{N}{8\pi g V} \left( \frac{ch}{kT} \right)^3 = A \left( 1 + \frac{6}{\alpha^2} + \frac{135}{\alpha^4} + \dots \right) - \frac{A^2}{8} \left( 1 + \frac{3}{2\alpha^2} + \frac{135}{16\alpha^4} + \dots \right) \quad (33)$$

Inverting the series (33) we have

$$A = A_0 \left\{ 1 - \frac{6}{\alpha^2} \left( 1 + \frac{7}{32} A_0 \right) \right\}, \quad (34)$$

where  $A \rightarrow A_0$  when  $\alpha \rightarrow \infty$

In the relativistic case, energy  $E$  is given by

$$\begin{aligned} E &= \frac{4\pi g V}{c^3 h^3} \int_0^{c_1} \frac{\epsilon^2 d\epsilon}{\left( 1 - \frac{\epsilon^2}{b^2 c^2} \right)^{\frac{1}{2}} \left( 1 + \frac{1}{A} e^{\epsilon/kT} \right)} \\ &= \frac{4\pi g V b^4 c^4}{c^3 h^3} \int_0^1 \frac{u^3}{(1-u^2)^{\frac{1}{2}}} \left\{ A e^{-\alpha u} - A^2 e^{-2\alpha u} + \dots \right\} du \end{aligned} \quad (35)$$

But 
$$\int_0^1 \frac{t^2 e^{-xt} dt}{(1-t^2)^{\frac{1}{2}}} = \frac{6}{x^4} + \frac{60}{x^6} + \dots \quad \text{when } x \rightarrow \infty, \quad (36)$$

therefore

$$E = \frac{kTNA}{\beta} \left( 3 + \frac{30}{\alpha^2} - \frac{3A}{16} - \frac{15A}{32\alpha^2} \right), \quad (37)$$

where  $\beta = \frac{N}{8\pi g V} \left( \frac{ch}{kT} \right)^3$

Evaluating the integral and substituting the values of  $E$  and  $A$  in (22), we have

$$TS = \frac{kTNA}{\beta} \left\{ 4 + 36 \left( \frac{kT}{bc} \right)^2 - \frac{A}{4} - \frac{9A}{16} \left( \frac{kT}{bc} \right)^2 \right\} - NkT \log A \quad (38)$$

From (27), (37), and (38), we have the value of  $G$

$$G = \frac{kTNA}{\beta} \left( \frac{4}{\alpha^2} - \frac{A}{16\alpha^2} \right) + NkT \log A \quad (39)$$

In the non-relativistic case, we have from (3),

$$N = \frac{4\pi g V b^3}{h^3} \int_0^1 \frac{u^2}{(1-u^2)^{\frac{1}{2}}} \left\{ A e^{-\alpha u^2} - A^2 e^{-2\alpha u^2} + \dots \right\} du, \quad (40)$$

where  $\epsilon = \frac{b^2 u^2}{2m}$ , and  $\alpha = \frac{b^2}{2mkT}$ .

But when  $\alpha \gg 1$

$$\int_0^1 \frac{u^2}{(1-u^2)^{\frac{1}{2}}} e^{-\alpha u^2} du = \frac{\pi^{\frac{1}{2}}}{4\alpha^{\frac{1}{2}}} \left( 1 + \frac{3}{4\alpha} + \frac{45}{32\alpha^2} + \dots \right) \quad (41)$$

Therefore

$$N = \frac{gV}{h^3} (2\pi mkT)^{\frac{1}{2}} A \left\{ \left( 1 + \frac{3}{4\alpha} + \frac{45}{32\alpha^2} \right) - \frac{A}{2^{\frac{1}{2}}} \left( 1 + \frac{3}{8\alpha} \right) \right\} \quad (42)$$

Inverting the series we get

$$A = A_0 \left\{ 1 - \frac{3}{4\alpha} \left( 1 + \frac{3A_0}{4 \cdot 2^{\frac{1}{2}}} \right) \right\}, \quad (43)$$

where  $A_0$  is the value of  $A$  when  $\alpha \rightarrow \infty$   $\left( A_0 = \frac{N h^3}{gV(2\pi mkT)^{\frac{1}{2}}} \right)$

In the non-relativistic case, energy is

$$E = \frac{4\pi gV}{h^3} \frac{b^5}{2\pi} \int_0^1 \frac{u^4}{(1-u^2)^{\frac{1}{2}}} \{ A e^{-\alpha u^2} - A^2 e^{-2\alpha u^2} + \dots \} du \quad (44)$$

$$= \frac{3AkTgV}{2h^3} (2\pi mkT)^{\frac{1}{2}} \left\{ \left( 1 + \frac{5}{4\alpha} + \frac{105}{32\alpha^2} \right) - \frac{A}{4 \cdot 2^{\frac{1}{2}}} \left( 1 + \frac{5}{8\alpha} + \frac{105}{128\alpha^2} \right) \right\} \quad (45)$$

From (22) and (45) we obtain the expression for entropy

$$TS = \frac{kTgV}{h^3} (2\pi mkT)^{\frac{1}{2}} A \left\{ \left( \frac{5}{2} + \frac{21}{8\alpha} + \frac{405}{64\alpha^2} \right) - \frac{A}{4 \cdot 2^{\frac{1}{2}}} \left( \frac{5}{2} + \frac{21}{16\alpha} + \frac{405}{256\alpha^2} \right) \right\} - NkT \log A \quad (46)$$

Gibb's free energy is given by

$$G = AkTgV(2\pi mkT)^{\frac{1}{2}} \left\{ \frac{1}{2\alpha} + \frac{15}{8\alpha^2} - \frac{A}{4 \cdot 2^{\frac{1}{2}}} \left( \frac{1}{4\alpha} + \frac{15}{32\alpha^2} \right) \right\} + NkT \log A \quad (47)$$

We have calculated thermodynamic functions for the non-degenerate case when  $\alpha \gg 1$ . We now calculate them when  $\alpha \ll 1$ . Equation (31) gives when  $\alpha \ll 1$

$$\frac{N h^3}{\pi^2 g V b^3} = A \left( 1 - \frac{8\alpha}{3\pi} - A \right) \quad (48)$$

Inverting the series (48) we get

$$A = A_0 \left( 1 + \frac{8\alpha}{3\pi} \right), \quad (49)$$

where  $A \rightarrow A_0$  when  $\alpha \rightarrow 0$

Energy  $E$  is given by

$$\begin{aligned} E &= \frac{4\pi gV b^4 c^4}{c^3 h^3} \int_0^1 \frac{u^3}{(1-u^2)^{\frac{1}{2}}} (A e^{-\alpha u} - A^2 e^{-2\alpha u} + \dots) du, \\ &= \frac{8A\alpha kT V \pi g b^3}{3h^3} \left( 1 - \frac{9\pi\alpha}{32} - A \right). \end{aligned} \quad (50)$$

From (22) and (50) we have

$$TS = \frac{kT b^3 \pi^2 g V A}{h^3} \left( 1 - \frac{A}{2} - \frac{3\alpha^2}{8} \right) - kTN \log A \quad (51)$$

Gibb's free energy is

$$G = \frac{\pi^2 kT g V b^3 A}{h^3} \left( \frac{32\alpha}{9\pi} - \frac{5\alpha^2}{8} - 1 + \frac{A}{2} - \frac{32A\alpha}{9\pi} \right) + NkT \log A \quad (52)$$

Lastly we proceed to the non-relativistic non-degenerate case when  $\alpha \ll 1$ . We have from (40) when  $\alpha \ll 1$

$$\frac{N\hbar^3}{\pi^2 g V b^3} = A \left( 1 - \frac{3\alpha}{4} + \frac{15\alpha^2}{48} \right) - A^2 \left( 1 - \frac{3\alpha}{2} \right) \quad (53)$$

Inverting the series (53) we have

$$A = A_0 \left( 1 + \frac{3\alpha}{4} \right), \quad (54)$$

where  $A \rightarrow A_0$  when  $\alpha \rightarrow 0$

From (44) energy is given by

$$E = \frac{3A\alpha\pi^2 g V b^3 kT}{4\hbar^3} \left\{ 1 - \frac{5\alpha}{6} + \frac{35\alpha^2}{96} - A \left( 1 - \frac{5\alpha}{3} + \frac{35\alpha^2}{24} \right) \right\} \quad (55)$$

From (22) and (55) we have

$$TS = \frac{\pi^2 g V b^3 kT A}{\hbar^3} \left( 1 - \frac{5\alpha^2}{16} - \frac{A}{2} \right) - NkT \log A, \quad (56)$$

Gibb's free energy is given by the equation

$$G = \frac{\pi^2 g b^3 kT A V}{\hbar^3} \left( \frac{5\alpha}{4} - 1 + \frac{A}{2} - \frac{35\alpha^2}{48} \right) + NkT \log A \quad (57)$$

Our grateful thanks are due to Dr D S Kothari, Professor of Physics, University of Delhi, for his interest in the work

#### APPENDIX

The various integrals for energy, pressure, and entropy are of the form

$$\int_0^\alpha \frac{d\phi(u)}{\left( 1 - \frac{u^2 + 2uy}{\alpha^2 + 2\alpha y} \right)^{\frac{1}{2}} (1 + e^{u-u_0})},$$

where  $\phi'(0) = 0$  and  $\alpha$ ,  $y$  and  $u_0$  are constants.  $y$  and  $\alpha$  are positive and  $y = \frac{mc^2}{kT}$ . An asymptotic expansion of the above integral subject to an error of  $e^{-u_0}$  can be found for the case when  $u_0 \gg 1$ .

Consider the integral

$$\begin{aligned} \int_0^\alpha \frac{d\phi(u)}{\left( 1 - \frac{u^2 + 2uy}{\alpha^2 + 2\alpha y} \right)^{\frac{1}{2}} (1 + e^{u-u_0})} &= \int_0^{u_0} \frac{d\phi(u)}{\left( 1 - \frac{u^2 + 2uy}{\alpha^2 + 2\alpha y} \right)^{\frac{1}{2}} (1 + e^{u-u_0})} \\ &+ \int_{u_0}^{\theta\alpha} \frac{d\phi(u)}{\left( 1 - \frac{u^2 + 2uy}{\alpha^2 + 2\alpha y} \right)^{\frac{1}{2}} (1 + e^{u-u_0})} + \int_{\theta\alpha}^\alpha \frac{d\phi(u)}{\left( 1 - \frac{u^2 + 2uy}{\alpha^2 + 2\alpha y} \right)^{\frac{1}{2}} (1 + e^{u-u_0})}, \end{aligned}$$

$\theta$  being a proper fraction. Also

$$\int_0^{u_0} \frac{d\phi(u)}{\left( 1 - \frac{u^2 + 2uy}{\alpha^2 + 2\alpha y} \right)^{\frac{1}{2}} (1 + e^{u-u_0})} = \int_0^{u_0} \frac{d\phi(u)}{1 + e^{u-u_0}} \left\{ 1 + \frac{1}{2} \frac{u^2 + 2uy}{\alpha^2 + 2\alpha y} + \right\}$$

Now

$$\begin{aligned}\int_0^{u_0} \frac{d\phi(u)}{1+e^{u-u_0}} &= \phi(u_0) - \int_0^{u_0} \frac{\phi'(u)e^{u-u_0} du}{1+e^{u-u_0}} \\ &= \phi(u_0) - \int_0^{u_0} \phi'(u) \{e^{u-u_0} - e^{-2(u-u_0)} + \dots\} du \\ &= \phi(u_0) - C_1 \phi'(u_0) + C_2 \phi''(u_0) - \dots + O(e^{-u_0})\end{aligned}$$

where  $C_{2n} = (1-2^{1-2n})\zeta(2n)$ ,  $\zeta(2n)$  being the Riemann-zeta function. The numerical values of  $C_{2n}$  are (McDougall and Stoner, 1938)

$$C_2 = \frac{\pi^2}{12} = 0.82247, \quad C_4 = \frac{7\pi^4}{720} = 0.947032$$

$$\begin{aligned}\int_{u_0}^{\theta\alpha} \frac{d\phi(u)}{1+e^{u-u_0}} &= \int_{u_0}^{\theta\alpha} \phi'(u) \{e^{u-u_0} - e^{2(u-u_0)} + \dots\} du \\ &= C_1 \phi'(u_0) + C_2 \phi''(u_0) + \dots + O(e^{u_0-\theta\alpha}) \\ \int_{\theta\alpha}^{\alpha} \frac{d\phi(u)}{\left(1 - \frac{u^2+2uy}{\alpha^2+2\alpha y}\right)^{\frac{1}{2}} (1+e^{u-u_0})} &= \int_{\theta\alpha}^{\alpha} \frac{(\alpha^2+2\alpha y)^{\frac{1}{2}} \phi'(u) du}{\{(\alpha+y)^2 - (u+y)^2\}^{\frac{1}{2}} (1+e^{u-u_0})} \\ &= \left\{ \sin^{-1} \frac{u+y}{\alpha+y} \frac{(\alpha^2+2\alpha y)^{\frac{1}{2}} \phi'(u)}{1+e^{u-u_0}} \right\}_{\theta\alpha}^{\alpha} \\ &\quad - (\alpha^2+2\alpha y)^{\frac{1}{2}} \int_{\theta\alpha}^{\alpha} \sin^{-1} \frac{u+y}{\alpha+y} \left\{ \frac{\phi''(u)}{1+e^{u-u_0}} - \frac{\phi'(u)e^{u-u_0}}{(1+e^{u-u_0})^2} \right\} du\end{aligned}$$

$$\text{The 1st term} < \frac{\frac{\pi}{2} (\alpha^2+2\alpha y)^{\frac{1}{2}} \phi'(\alpha)}{1+e^{\alpha-u_0}} < \frac{\pi}{2} (\alpha^2+2\alpha y)^{\frac{1}{2}} \phi'(\alpha) e^{u_0-\alpha}$$

$$\begin{aligned}\text{The 2nd term} &< (\alpha^2+2\alpha y)^{\frac{1}{2}} \frac{\pi}{2} \int_{\theta\alpha}^{\alpha} \left\{ \frac{\phi''(u)}{1+e^{u-u_0}} - \frac{\phi'(u)e^{u-u_0}}{(1+e^{u-u_0})^2} \right\} du \\ &= (\alpha^2+2\alpha y)^{\frac{1}{2}} \frac{\pi}{2} \int_{\theta\alpha}^{\alpha} \frac{d}{du} \left( \frac{\phi'(u)}{1+e^{u-u_0}} \right) du \\ &= (\alpha^2+2\alpha y)^{\frac{1}{2}} \frac{\pi}{2} \left\{ \frac{\phi'(\alpha)}{1+e^{\alpha-u_0}} - \frac{\phi'(\theta\alpha)}{1+e^{\theta\alpha-u_0}} \right\} \\ &= O(e^{-u_0}).\end{aligned}$$

Thus if  $u_0 \ll \alpha$  we have the asymptotic expansion

$$\int_0^{\alpha} \frac{\phi'(u) du}{1+e^{u-u_0}} = \phi(u_0) + 2C_2 \phi''(u_0) + 2C_4 \phi^{(iv)}(u_0) + \dots + O(e^{-u_0}).$$

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ON A NEW COCCIDIUM, *EIMERIA HIMALAYANUM* N Sp.,  
FROM THE INTESTINE OF A HIMALAYAN TOAD,  
*BUFO HIMALAYANUS* BOULENGER<sup>1</sup>

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In March 1940, one of the writers, while examining the gut contents of a toad, came across a species of coccidium. A perusal of the available literature showed that, although six species of *Eimeria* had previously been recorded from the intestine of anurous amphibians, this particular one did not correspond with any known before. These six species are *Eimeria ranarum* Labbé (1894), *E. (Paracoccidium) prevoti* Laveran and Mesnil (1903), *E. ranæ* Dobell (1908), *E. neglecta* Nöller (1920), *E. belawan* Yakimoff (1930), and *E. laminata* Ray (1935). *E. ranarum* inhabits the nuclei and some stages of others have been found in the cytoplasm of the epithelial cells or free in the lumen of the guts. Furthermore, except in the case of *E. laminata* Ray (1935), the complete life-history has not been described in any of these species. In *E. laminata*, the asexual forms and their young products have a remarkable activity: schizogony is initiated at a very early stage and there are two kinds of schizonts, namely, (a) macroschizonts, releasing 20-30 merozoites which develop into macrogametes, and (b) micros schizonts, producing six to eight merozoites which become male and give rise to numerous microgametes.

The endogenous stages of the new coccidium exhibited certain differences from those described by Ray (1935) in *E. laminata*. The whole life-cycle, including the formation of mature spores, was found to occur in the epithelial cells of the small intestine. Whether this peculiarity is the outcome of adaptation to the rigour of the climatic conditions of Mukteswar (altitude 7,500 ft) it is difficult to say.

Although the material for the present study came from a single specimen, it so happened that schizogony and sporogony were found to occur simultaneously in the specimen and consequently it was possible to obtain all essential information from this limited source.

#### METHODS.

As the rectal contents of this toad revealed a few mature oöcysts, a few smears were made from this part in order to study the endogenous stages, if any, of the coccidium. Portions of infected intestine were fixed overnight in Bouin Duboscq and Brasil's fluid while smears were fixed for 20 minutes in Schaudinn's fluid. The stains used were Delafield's and Heidenhain's hæmatoxylin. Sections of the intestine were cut 6  $\mu$  thick. The living parasite was studied in sealed preparations of the rectal and intestinal contents diluted with normal saline solution.

#### OBSERVATIONS ON THE FREE FORMS OF THE COCCIDIUM

In fresh preparations there were seen a few active 'gregarulæ', which showed a bowing movement like that of the gregarine *Selenidium*. At first it was thought possible that the species was *E. laminata* but closer observation revealed that these 'gregarulæ' were devoid of the hyaline blade-like structure or lamina, so characteristic of *E. laminata*. In a fresh smear certain stages, which were considered to be developing microgametes,

<sup>1</sup> Paper read at the 28th session of the Indian Science Congress, held at Benares in 1941

were encountered. It should be mentioned that the number of microgametes formed was very small, as compared with that of other Eimeriids,—a fact confirmed by a study of the smears and sections. In fresh samples of rectal contents stages other than fully mature oöcysts were not encountered.

#### MICROSCHIZOGONY AND FORMATION OF MICROGAMETES

In the fixed and stained material, schizonts, that would give rise to the male parasites, could not at first be readily distinguished from the other type which produces macromerozoites. A prolonged search, however, showed that while the cytoplasm of the smallest microschizont, measuring about  $1.8\ \mu$  to  $2.17\ \mu$  in diameter, presented a ragged appearance with a faintly developed nuclear membrane (Pl II, fig 2), a macroschizont, measuring  $5.21\ \mu$  in diameter, showed a homogeneous cytoplasmic structure with a prominent nuclear membrane (Pl II, fig 1a). A microschizont may either remain distally to the nucleus of the epithelial cell or pass beyond it towards the basement-membrane to complete the schizogony. About 16–32 merozoites are formed, each of which measures nearly  $4.6\ \mu$  in length and  $0.4\ \mu$  in width. A fully formed micromerozoite shows a more or less ragged cytoplasm and a deeply staining area at one pole (Pl II, fig 4). In this respect it appears to differ from the macromerozoite which never shows such a siderophilous structure.

A micromerozoite, which produces microgametes, develops to about  $6.8\ \mu$  in diameter. The nucleus appears to divide into eight small nuclei which travel towards the periphery of the cytoplasm. The nuclear membrane, however, is not visible at any stage, although a clear halo is often seen surrounding the deeply stained nucleus. At a later stage small cytoplasmic elevations develop round each nucleus, while the nuclei are seen to be drawn towards the pointed ends of these elevations (Pl II, fig 11). Finally, the microgametes, measuring  $2.6\ \mu$  in length and  $0.86\ \mu$  in width, are differentiated (Pl II, fig 12). A fully formed microgamete shows a clear round or oval cytoplasmic area and a pointed nuclear zone. It was not possible to ascertain whether the microgametes are provided with any locomotory organ or not. On few occasions microgametes were seen entering the epithelial cells (Pl II, fig 10b). Unused microgametes were invariably found to degenerate with the maturation of the oöcyst (Pl II, figs. 6, 8, 9 and 13).

#### MACROSCHIZOGONY AND FORMATION OF MACROGAMETES.

In contrast to the microschizont, the macroschizont, i.e. those that will give rise to female parasites, have from a very early stage a homogeneously staining cytoplasm with a central nucleus surrounded by a prominent nuclear membrane and also provided with a karyosome. A fully grown macroschizont, whether below or beyond the nucleus of the host cell, measures about  $10\ \mu$  to  $12\ \mu$  in diameter and contains as many as 32 elongated merozoites. No sign of precocious nuclear division, as described for the merozoites of *E. laminata*, was encountered. A fully formed macromerozoite, measuring  $4.3\ \mu \times 0.65\ \mu$ , shows a homogeneously staining cytoplasm and a centrally situated nucleus with a central karyosome (Pl II, fig 3). This morphological differentiating character made it possible to distinguish micromerozoite from macromerozoite.

A fully grown female parasite measures about  $7\text{--}12\ \mu$  in length and  $6\text{--}10\ \mu$  in width; its cytoplasm shows an alveolar structure and is devoid of any inclusions. In this respect it differs from *E. laminata* which shows many irregular inclusions staining deeply with haematoxylin. The nucleus at this stage is spherical and has a diameter of about  $3\text{--}5\ \mu$ ; the nuclear membrane is very thin and there is no staining substance other than the karyosome. At a later stage the nuclear membrane becomes irregular in outline and the nucleus gives the impression of the formation of a 'fertilisation spindle' parallel to the long axis of the body.

#### SPOROLOGY.

Sporogony is strictly intracellular as is described for *E. laminata*. Unfertilised macrogametes lying within the host-cells are often seen to be surrounded by a number of micro-

gametes similar to those described above. On one occasion, however, as shown in fig 5 on Pl II, a stage which, it is believed, demonstrates the entry of the microgamete into the cytoplasm of the macrogamete, was encountered. The nuclear membrane of the macrogamete at this stage appears to have completely dissolved, while the karyosome is broken up into several minute granules. The unused microgametes are often seen to remain attached to the oöcyst membrane and finally degenerate (Pl II, figs 5-10 and 13). The cytoplasm of the zygote shows a deposit of minute refringent granules at the periphery and this at once distinguishes it from an unfertilised female parasite. The next stage encountered is shown in fig 8 on Pl II. It represents the zygote nucleus at the metaphase stage. Two centrosomes at either pole of the spindle are well marked, while at the equatorial region four dot-like chromosomes can be clearly made out. The zygote nucleus at the telophase stage was seen a number of times but on one occasion only was it possible to distinguish the chromosome number as mentioned above (Pl II, fig 9). The haploid number in this coccidium, then, appears to be two. The next stage found in abundance is the oöcyst with its contents divided to give rise to four sporoblasts. The oöcyst is rounded oval in shape and measures 7-10  $\mu$  along its broadest diameter. There is no oöcystic residue. The oöcystic wall, unlike that in other species of *Eimeria*, is very thin and often the double contour is not visible. In other *Eimeria*, where oöcysts mature extracorporally, formation of a tough membrane is perhaps a necessity and arises in response to environmental conditions. But, in this case, since maturation is intracellular, external factors play no part and, therefore, the oöcystic membrane is ill developed. It is not, however, known whether the mature oöcysts eliminated by the host can withstand the climatic conditions of Mukteswar. The naviculoid sporocysts measure about 5  $\mu$  in length and 2.8  $\mu$  in width, each contains two sporozoites and a residual body. The sporozoites measure 4.0  $\mu \times 1.4 \mu$ , are club-shaped and show siderophilous structures at either pole. These stain deeply with Heidenhain's iron-haematoxylin (Pl II, fig 14). The nucleus is situated at the centre of the club-shaped body and shows a karyosome surrounded by a nuclear membrane. On a few occasions sporozoites were found lying freely within the oöcyst, a characteristic similar to that observed in *E. prevoti*. There was no proof, however, of autoinfection. It is quite possible that, under certain abnormal conditions, the sporocystic membranes give way within the oöcyst and thus liberate the sporozoites.

#### CONCLUSIONS

The dizoic tetrasporocystid conditions of the oöcyst at once places this coccidium in the genus *Eimeria*. In the accompanying table a comparison is given on the species of *Eimeria* in respect of oöcyst and sporocyst. It will be seen that the form and dimensions of these bodies are sufficiently characteristic in this second coccidium of anurous amphibians from India to warrant our considering it a new species. We give the specific name *himalayanum* to denote its geographical occurrence.

Other features of interest may be summarised as follows —

There are two kinds of schizonts: (a) macroschizonts, releasing about thirty-two macromerozoites which develop into macrogametes, and (b) microschorizonts, producing about the same number of micromerozoites which become males and give rise to eight small microgametes—a number which is quite unlike that of any other species of *Eimeria*. Whether this peculiarity is the outcome of a prolonged intracellular habit of the parasite is very difficult to say at this stage of the enquiry but such an adaptation may possibly play an important rôle in bringing about this modification. Furthermore, it is due to this intracellular habitat and maturation of the oöcyst that its wall has become much less conspicuous than that of those *Eimeria* which have an extracorporal maturation.

#### DIAGNOSIS.

*Systematic position* *Eimeria himalayanum* n.sp. (Coccidiida, Eimeriidae)

*Description* Oöcysts rounded oval, without micropyle, residue absent; oöcystic membrane thin, 7-10  $\mu$  along its broadest diameter; sporocysts naviculoid, 5.2  $\mu \times 2.8 \mu$ ,

Table showing comparisons of the species of *Eimeria* in frog

Name.	Oöcyte			Sporooöcyte			Host	Locality
	Form	Size in microns	Rea- due	Form	Size in microns	Rea- due		
<i>E. ramana</i> Labbé, 1894	Oval	17 × 12	—	Fusiform	7 × 4	+	<i>Rana temporaria</i> <i>R. esculenta</i>	France
<i>E. prevoti</i> Laveran and Mauri, 1902	Oval	20-22 × 12-15	+	Oval	?	+	<i>R. esculenta</i>	France
<i>E. ramus</i> Dobell, 1908	Rounded oval.	18-22	+	Naviculoid	14 × 7	—	<i>R. temporaria</i> <i>R. esculenta</i>	England (Cambridge) Germany (Munich).
<i>E. neglecta</i> Noller, 1920	Round	9-10	—	Oval	7 × 4	+	<i>R. temporaria</i> <i>R. esculenta</i>	Germany (Hamburg).
<i>E. belakovi</i> Yakimoff, 1920	Round	12-21	—	Round	4-44	+	<i>Hyla arborea</i>	North Caucasus (Pjatigorsk)
<i>E. lamata</i> Ray, 1935	Spherical	8-11	—	Fusiform	4-5-8	+	<i>Bufo melanostictus</i>	India (Calcutta)
<i>E. himalayensis</i> , n.sp.	Rounded oval	7-10	—	Naviculoid	5-2 × 2-8	+	<i>Bufo himalayensis</i>	India (Mukteswar- Kumaun, U.P.).

sporozoites club-shaped with a siderophilous structure at either pole; mature oöcysts discharged from host, macro- and microschizonts giving rise to female and male gametes respectively, eight male gametes produced from each micromerozoite

*Habitat* Small intestine (intracellular) of *Bufo himalayensis* Boulenger (Amphibia, Anura)

*Locality* Mukteswar-Kumaun, U P, India.

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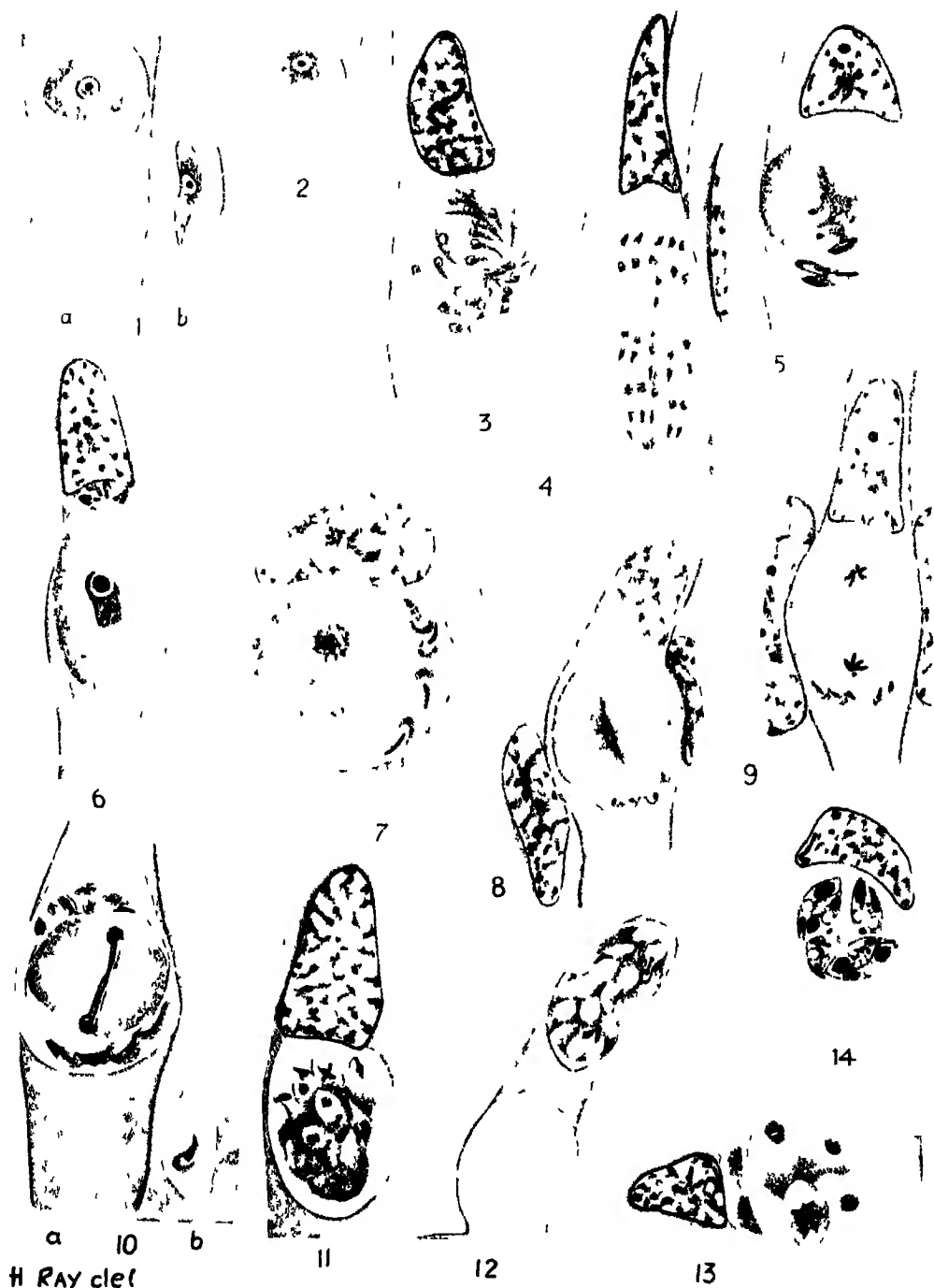
#### EXPLANATION OF PLATE

All figures from sections except fig 7, magnification  $\times 2,300$

- Fig 1 a and b Growing female trophozoites  
 Fig 2 Growing male trophozoite  
 Figs 3 and 4 Macro and micro merozoites  
 Fig 5 Macrogamete with one microgamete lying in the 'fertilisation spindle' while two others are abutting on the 'fertilisation cone'  
 Fig 6 Oöcyst with four microgametes lying in the same vacuole  
 Fig 7 Same as above Taken from a smear  
 Figs 8-10a Oöcysts in metaphase, telophase and late telophase respectively Note the degenerating microgametes  
 Fig 10b A microgamete lying within the epithelial cells  
 Figs 11 and 12 Developing microgametes  
 Fig 13 Sporoblast formation, note the degenerating microgametes lying within the same vacuole  
 Fig 14 Mature oöcyst

N.B.—Double contour of the oöcystic membrane is visible only in figs 7 and 9







# THE SPERMATOGENESIS OF *ICHTHYOPHIS GLUTINOSUS* LINN

## PART 3 SPERMATELEOSIS

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### INTRODUCTION

There is no reference in literature regarding the formation of the spermatozoon in the Apoda (Amphibia), while in the Urodela and Anura, this subject has been dealt with at great length. In fact, next to insect spermateleosis, the best known is that of Urodela and the importance of the subject may be judged by the fact that even till recently studies on the sperm formation in urodeles revealed new facts regarding the phenomenon.

The interest regarding spermateleosis lies in the fact that it relates mainly to the activity and transformations of the extra-nuclear bodies in the cell,—especially the centrosome, the Golgi apparatus and the mitochondria, which construct and shape the future sperm. The history of the development of the spermatozoon from the spermatid is chiefly the history of the cytoplasmic bodies.

In the Amphibia the spermateleosis of only the Urodela and Anura is known. That of the Apoda has never before been studied and it is the purpose of this paper to present the sequence of events in sperm formation in *Ichthyophis glutinosus*, a South Indian species of Apoda. The earlier studies of the spermatogenesis of this animal have formed the subject matter of the first two parts already published by me (1936, 1937).

The material for this study has been fixed and stained in various ways, a more detailed description of which has been given by me in the first part of this work (1936). Smears of the testis have also been made and fixed in Champy, Flemming, Mann-Kopsch, Bouin and Kolatchew fluids. Another useful method of examination has been that adopted by Snook and Long (1914) in their studies on *Aneides lugubris* and has proved very advantageous with material fixed, especially in Mann-Kopsch and Kolatchew fluids. The testis lobes were fixed and treated in the usual manner but in xylol, the material which showed signs of brittleness, was lightly crushed and teased on a slide which was now treated like a smear. As a result of this process the cells are not liable to become distorted, and though while crushing, a few cell elements become broken up, a very large number of them remain intact and lend themselves to easy examination. I have found this method particularly useful and advantageous in respect of material fixed in one of the osmic fluids, and apart from a few spermatozoa which have become broken up, the other stages are particularly well seen and have formed helpful adjuncts to sections and smears.

I have great pleasure in thanking Prof A Subba Rau for his many useful suggestions and criticisms during the course of this study.

### PREVIOUS WORK

The earliest account of the sperm of *Ichthyophis glutinosus* is that of the Sarasins (1890) who have figured the spermatozoon of this animal. But their figures are so incomplete and their description so meagre that Ballowitz (1913) in reviewing the then available knowledge of the structure and development of the animal sperm, denies all knowledge of the sperms of Apoda. No other detailed examination of either the structure

or the formation of the sperm has been made till now and the easy availability of the material has alone been responsible for my being able to study the development of the spermatozoon in *Ichthyophis glutinosus*

Our knowledge of the spermatogenesis of the Urodela and the Anura on the other hand is fairly extensive and complete and has been admirably summarised by Wilson (1928). Curiously the sperms of these two groups of Amphibia fall under two different categories, that of the Anura being simpler and more typical. Apart from the acrosome whose form, size and shape are subject to variation within each group, the differences lie in the important constituents of the sperms. In the Anura, the head is followed by a distinct neck region, in which both the centrioles are lodged, one behind the other. From the distal one starts the flagellum which may possess an undulating membrane as in *Alytes* (Retzius, 1906), *Bufo* (King, 1907), *Bombina* (Broman, 1900, Champy, 1913) and *Discoglossus* (Champy, 1923), or the undulating membrane may be wanting as in *Rana* (Broman, 1907, Champy, 1913), *Hyla* (Retzius, 1906) and *Pelobates* (Broman, 1901).

The base of the flagellum in a number of genera is ensheathed by mitochondrial granules which assume a spiral structure and this region is designated the 'middle piece'. This mitochondrial sheath may be conspicuous as in *Rana fusca* (Broman, 1907) or may be small and rounded as in *Rana nigromaculata* (Morita, 1928), *Rana mugiens* and *Rana arvalis* (Wilson, 1928). Posteriorly the flagellum is free.

Compared with this simple sperm of Anura that of the Urodela assumes a unique complexity, in many respects offering examples of the most advanced type found in animals. In the urodele sperm (Meves, 1897, Macgregor, 1899, Terni, 1911, Champy, 1913, Bowen, 1922, Gatenby, 1931), the base of the head is occupied by a very much enlarged and elongated proximal centriole. Posterior to the proximal centriole lies the distal centriole, which, like the proximal centriole, undergoes a modification, but in quite a different manner. It is converted into a ring which becomes greatly elongated and which lies along the greater part of the flagellum as a long pessary. The mitochondria are generally absent from the adult urodele sperm.

Into this picture of the very divergent form and constitution of the Anuran and Urodelan sperms has to be fitted the sperm of the other group of Amphibia, namely the Apoda, and the first attempt may be made by a study of the ripe sperm of *Ichthyophis glutinosus*.

#### OBSERVATIONS

##### *Ripe spermatozoon of Ichthyophis glutinosus*

Fig. 23 represents the ripe sperm of *Ichthyophis glutinosus*. Its measurements, based on the average of twenty counts are as follows:

Total length.	..	110 microns
Length of acrosome		5 microns
Length of nucleus	.	8 microns
Length of 'middle piece'		5.5 microns.

It will be seen that the nucleus of the sperm is surmounted by an acrosome which has a characteristic form and shape. In *Ichthyophis* it has the conventional appearance of an ordinary electric bulb, with a narrow base and an enlarged and rounded end. In this shape and form of the acrosome the Apoda is an extremely well-knit group, for in a number of other genera I have examined, it has the same appearance. On the other hand, the Urodela and Anura exhibit a great variety of shape and form of the acrosome.

The nucleus of the sperm is followed by a very conspicuous area, about 5.5 microns in length, and which is the 'middle piece' of the sperm. In Bouin preparations it appears as a simple tubular sheath encircling and enclosing the base of the flagellum. In osmic preparations, however (Flemming, Champy, Mann-Kopsch and Kolatchew), the sheath contains a spiral coil of what are obviously mitochondrial granules enveloping the flagellar fibre (Fig. 22). It must be stated here that both the centrioles are in close contact with the nucleus at its posterior end and in a ripe spermatozoon, they can hardly be

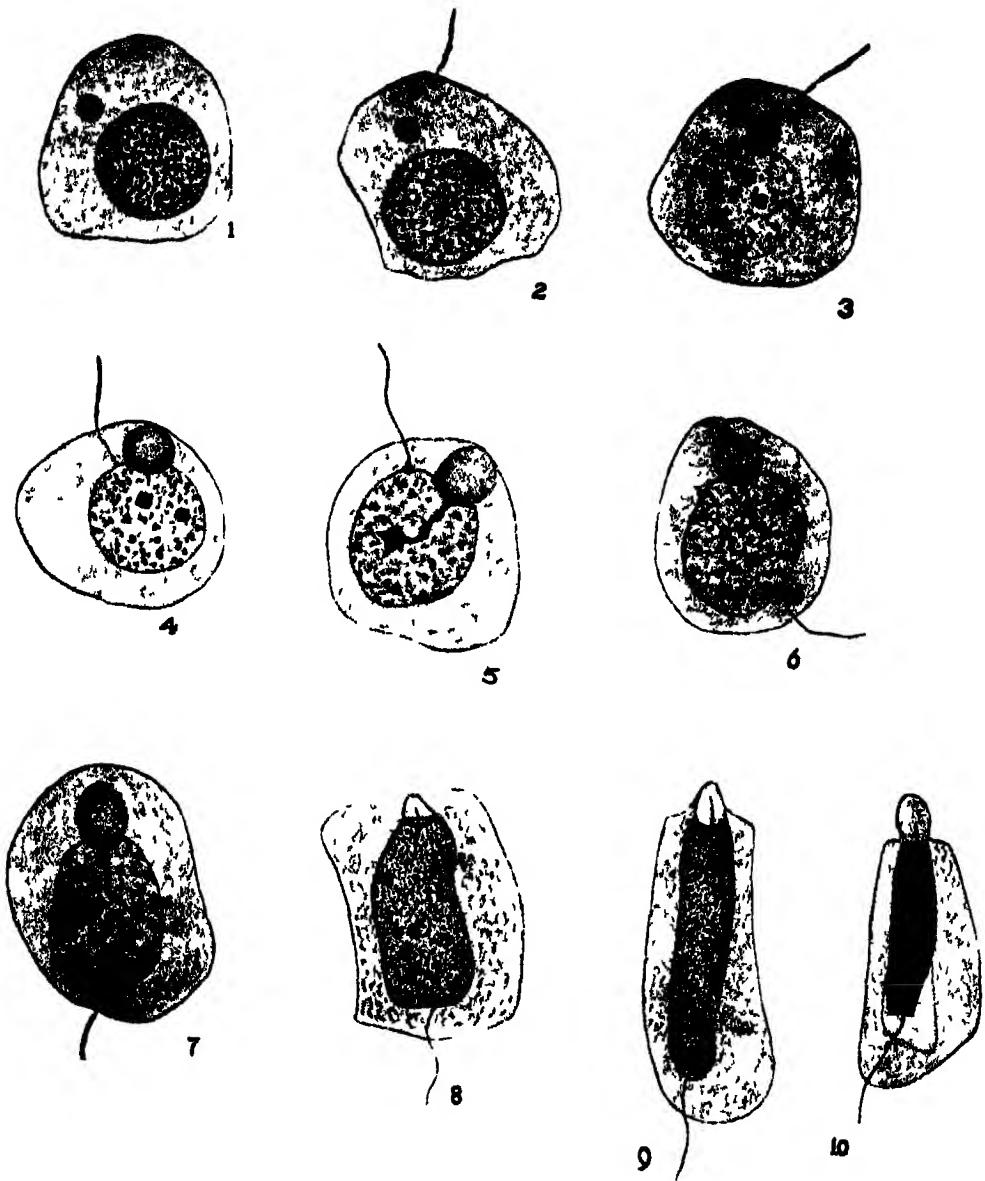


Fig 1. An early spermatid of *Ichthyophis glutinosus*. The sphere and the two centrioles are seen  $\times 2250$ . Fig 2. The two centrioles have migrated to the periphery of the cell and the distal one has just given off the filament.  $\times 2250$ . Fig 3. The sphere has planted itself on the nucleus and the beginning of the acrosome seat is formed as a deeply staining cup. The centrioles have started their inward movement.  $\times 2250$ . Fig 4. The acrosome vesicle is larger and is more firmly placed on the nucleus. The proximal centriole has come in contact with the nuclear wall.  $\times 2250$ . Fig 5. The acrosome seat is well formed. The rim of the cup as well as the deeply staining plug are seen. The proximal centriole has become flattened.  $\times 2250$ . Fig 6. A migration of the centrioles posteriorly towards their definitive position is seen.  $\times 2250$ . Fig 7. The acrosomic vesicle and the centrioles are now at the opposite poles of the nucleus. The proximal centriole has become a ring through which the distal one carrying the filament is moving inwards into the nucleus.  $\times 2250$ . Fig 8. The nucleus is becoming elongated. The acrosomic vesicle has developed a central filament. The centrioles are seen clearly in their definitive positions and relationships.  $\times 2250$ . Fig 9. Stage showing the maximum elongation of the nucleus. At this stage the nucleus exhibits poorest basophily.  $\times 2250$ . Fig 10. A contraction of the nucleus at its posterior end is seen. The disc-shaped proximal centriole is still clear and a nonstaining area separates it from the nucleus. The distal centriole has penetrated into the nucleus.  $\times 2250$ .

distinguished One of them (the proximal centriole, as will be seen later) has flattened into a disc-shaped ring and has applied itself to the base of the nucleus (Figs 10, 29) through the orifice of which, the other (the distal) centriole has entered and is embedded in the nucleus The 'middle piece', therefore, does not denote the region separated by the two centrioles or their derivatives, as in the mammals, but is simply that region of the base of the flagellum ensheathed by mitochondria and has no representative of either centriole in it

The flagellum is very long and bears the undulating membrane which begins behind the 'middle piece' and ends close to the tip of the flagellum

### *Spermateliosis*

I shall divide the history of the development of the spermatozoon of *Ichthyophis glutinosus* into five parts, each part dealing with the development of one cell structure

(a) *The centrioles*—An early spermatid of *Ichthyophis glutinosus* is shown in Fig 1 The nucleus shows a fine granulation characteristic of the early stages of the spermatid In Bouin preparations the centrioles may be seen close together enclosed in the sphere area between the nucleus and the cell border In osmic preparations such a stage would appear as in Fig 14 The Golgi-idiozome complex would appear in the same position as the sphere did in Bouin preparations and the Golgi bodies are seen as dark and discrete bodies The mitochondria occur as small granules scattered throughout the cell

The first change that occurs in the spermatid is an escape of the centrioles from the sphere region The two granules are now found outside the sphere but close to it In slightly later stages the centrioles, still keeping together, move towards the periphery of the cell Soon after, the two centrioles by their disposition with reference to the cell border can be distinguished as distal and proximal ones, for they are arranged in a plane at right angles to the cell border, with the distal centriole almost on the wall itself and the proximal one inwards in the cell The distal centriole soon gives off a filament which appears, therefore, for the first time in this stage (Fig 2)

The next change consists of an outward movement of the centrioles Still keeping together, the two centrioles leave their peripheral position in the cell and migrate inwards, the distal centriole carrying the filament also with it It is interesting to notice this continued association between the two centrioles throughout their history so far, first in their outward migration towards the cell periphery and then their return movement from the cell border towards the nucleus

Having arrived at the nucleus, the proximal centriole attaches itself to the nuclear wall This attachment at first takes place at any spot on the nuclear wall, but later, the centrioles migrate to the pole of the nucleus opposite to that where the acrosome is planted, which is the posterior pole In the early stages on the other hand, no such relation between the point of attachment of the centriole and the anterior pole of the nucleus can be made out A perusal of Figs 4-6 shows the varied positions where the attachment is effected in early stages, i.e., close to the acrosome, on the sides of the nucleus and posteriorly also In some cases, the proximal centriole is attached anteriorly But whatever be the early positions, the final position of attachment of the centriole is the posterior end of the now elongate nucleus (Fig 7)

The proximal centriole, as soon as it attaches itself to the nuclear wall, becomes enlarged and flattened Figs 5 and 6 show the attached proximal centriole much larger than the free distal one. Soon after its arrival posteriorly and once its definitive and final position is established, the proximal centriole becomes converted into a ring which is pressed to the posterior nuclear wall

As soon as the proximal centriole is fixed to the nucleus at its definitive posterior pole and is converted into a ring, the distal centriole moves forwards, becomes elongated and spindle-shaped, and, passing through the orifice of the ring-shaped proximal centriole becomes stuck to the nucleus Meanwhile the ring centriole becomes wider and better differentiated as the nucleus becomes narrower till finally the flattened ring marks the posterior end of the nucleus from out of the central orifice of which the filament passes out (Figs. 7-9),

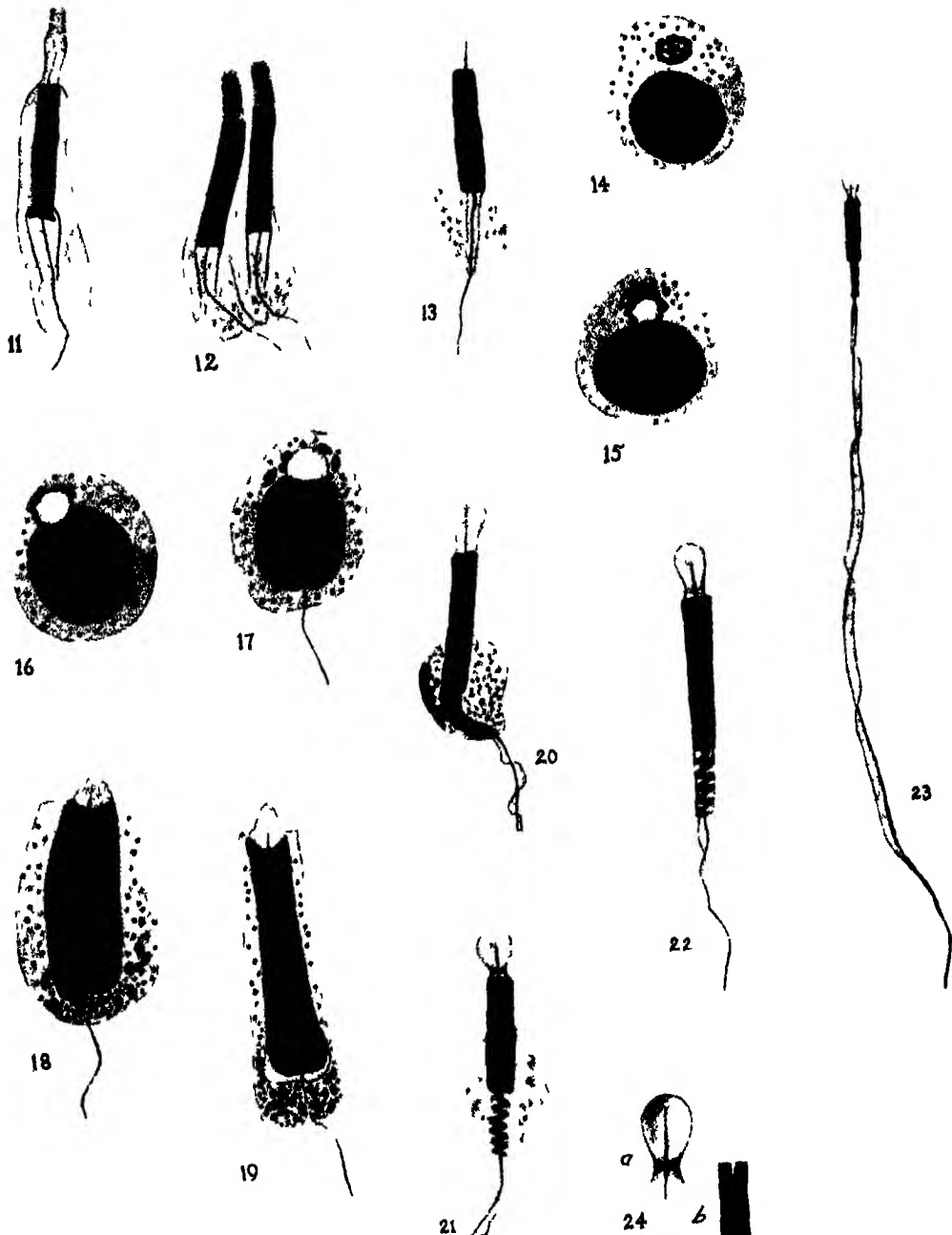


Fig. 11. The post-nuclear space has moved backwards and its wall forms the wall of the tubular sheath of the 'middle piece'.  $\times 2250$  Fig. 12. The tubular sheath is fully formed and granules, obviously mitochondria, are arranging themselves about the filament.  $\times 2250$ . Fig. 13. An almost fully developed sperm of *Ichthyophis glutinosus* with the residual protoplasm surrounding the posterior region of the nucleus and 'middle piece', the tubular sheath of which is seen clearly.  $\times 2250$  Fig. 14. An early spermatid of *Ichthyophis glutinosus* showing the initial position of the Golgi bodies and mitochondria.  $\times 2250$ . Fig. 15. The Golgi-idiosome complex has applied itself to the nucleus and the acrosome vesicle is developed. The Golgi bodies are arranged around it.  $\times 2250$ . Fig. 16. The acrosomic vesicle is planted in a cup-like depression in the nucleus and the deeply staining

plug is also seen.  $\times 2250$  Fig 17 Elongation of the nucleus and the beginning of the posterior migration of the Golgi bodies  $\times 2250$ . Fig 18 The Golgi bodies are all at the posterior pole. The plug of the acrosome seat is seen clearly with its dilated vesicular mouth  $\times 2250$  Fig 19 The greatest elongation of the nucleus has occurred and the nucleus has just begun to contract. The space formed as a result of it is seen.  $\times 2250$  Fig 20 An almost fully developed sperm of *Ichthyophis glutinosus* showing the Golgi bodies aggregated together in the sloughing off protoplasm  $\times 2250$  Fig 21 A sperm of *Ichthyophis glutinosus* with the residual protoplasm still in position. The mitochondrial spiral investment is seen. The acrosome has acquired its definitive shape  $\times 2250$  Fig 22 A ripe sperm of *Ichthyophis glutinosus* showing the acrosome, acrosome seat, nucleus and middle piece.  $\times 2250$ . Fig 23 A ripe sperm of *Ichthyophis glutinosus* showing its full length  $\times 1125$  Fig 24 Figures to show the form and structure of the acrosome (a) Acrosome (b) The anterior end of the nucleus showing the acrosome seat  $\times 3375$

In later stages where the nucleus of the spermatozoon is greatly condensed and consolidated, the proximal ring centriole has become a flattened plate completely incorporated in the nucleus and effectively fused with it so that it is practically impossible to distinguish the two, but in slightly earlier stages and with suitable fixatives, it is possible to notice the separation between the two,—the nucleus and the proximal centriole,—as a very narrow but nonstaining space (Figs 10, 20).

The proximal centriole in *Ichthyophis* is therefore closely applied to the nucleus posteriorly as a disc-like plate with an aperture in the centre through which the distal centriole with its filament passes into the nucleus and is embedded in it. This position of the two centrioles is the final one and is maintained in the adult spermatozoon without any change.

(b) *The acrosome*—The formation of the acrosome and its incorporation with the nucleus of the sperm have formed an important part of my studies of the spermatogenesis of *Ichthyophis* and I shall record here my observations of this process. In an early spermatid shown in Fig 14, from a Kolatchew preparation, the Golgi-idiozome complex is adjacent to the nucleus and in the same position as the sphere occupied in Bouin preparations. The Golgi bodies form a compact basketlike structure. The formation of the acrosome can be studied very well in Kolatchew preparations. Figs 15 and 31 illustrate Kolatchew preparations showing the acrosome formed in relation with the Golgi-idiozome complex. The acrosome is a clear vesicle round which are the dark Golgi bodies which have secreted it. It will be seen that the vesicle is occupying one pole of the nucleus. In fact, almost from the early stages of its formation the acrosomic vesicle is in close application with the wall of the nucleus at one of its poles. As development proceeds the acrosomic vesicle becomes more and more closely incorporated with the nucleus. This incorporation is one of the most interesting features of sperm formation.

The acrosome of the ripe sperm has already been described as a rounded bulbous body borne on a short narrow stalk. Figs 24a and 30 illustrate its form and shape. It is traversed in the centre by a fine filament which reaches almost to its tip and which is continued behind as a pointed plug about half the length of the acrosome. It is this plug that is placed in the nucleus of the sperm in a special receptacle in its centre. In sperms where the acrosome has become detached, this receptacle can be seen in the nucleus as a deep pit. The acrosome therefore gets its most effective anchor by means of this plug and pit arrangement, the former fitting into the latter. Posteriorly the acrosome is excavated into a shallow depression into which the anterior part of the nucleus fits, providing a further means of securing the two.

It has already been observed that the acrosome, almost from its inception, is close to the nuclear wall at one pole. In early stages no fusion or attachment between the two can be noticed but gradually the acrosome comes to be planted on the nucleus more firmly till in the final adult stage of the spermatozoon the two obtain a relationship just described. This incorporation of the acrosome with the nucleus takes place in relation to an acrosome seat which begins to be formed quite soon after the acrosomic vesicle is developed.

The acrosome seat is formed in the following manner: The acrosomic vesicle developed in the neighbourhood of the nucleus becomes closely pressed against its wall. The first trace of an acrosome seat is in the form of a shallow cup in the nucleus in which the

spherical acrosome is lodged (Fig 3) The rim of this cup is strengthened by a special fibre which stains deeply with haematoxylin From the rim arise a number of deeply stained strands which meet in a granule at the bottom centre of the cup In a polar view the acrosome seat now looks like a deeply staining ring from which three or four strands arise and meet in the central granule The whole structure can be compared to the rim, the hub and the spokes of a wheel, where the hub and the rim are not in the same plane, and where the former is at a lower level than the latter

In the next stage of its development a plug, also deeply stained, arises from the central granule of the cup and projects inwards into the nucleus This is clearly seen in Figs 4-7 and forms a conspicuous feature of the nucleus in early stages of spermatogenesis It is the most important part of the acrosome seat, for it is the fore runner of the deep pit in the nucleus of the ripe sperm into which the plug of the acrosome fits In Bouin-haematoxylin preparations, the plug is deeply stained In Mann-Kopsch and Kolatchew preparations it is seen as a dense streak running into the nucleus from the base of the shallow cup of the acrosome seat The further history of this pit is full of interest in Kolatchew preparations The streak soon becomes differentiated into a canal arising from the cup, projecting into the nucleus and ending blindly Sections passing across the nucleus at this region clearly show the canalicular nature of this organ and the lumen is also distinct But the most interesting fact is that in osmic preparations, especially in Kolatchew material, the wall of this canal becomes dark and can be distinctly seen I have photographed a spermatid showing this remarkable structure (Fig 32) It is from an unstained Kolatchew preparation The darkly stained wall of the pit with the cavity inside is clearly seen It will also be seen that at its mouth the pit becomes slightly dilated into a rounded vesicle whose wall also is osmicated What importance is to be attached to the darkening of the wall of the pit or the vesicular mouth, I am unable to say But that this pit is designed to lodge the plug of the acrosome, there is no doubt

At first the pit is long, but in later stages and with the progressive shortening and consolidation of the nucleus itself, the pit becomes shorter and in the fully developed sperm is seen as a blind canal extending some distance into the nucleus (Figs 22, 24) That this is intended for the lodgement of the lance-shaped plug of the acrosome, I have no doubt and that this pit and plug arrangement forms the most efficient means of cementing the acrosome to the nucleus I am convinced I am also convinced that, of the shallow cup and the deep pit that arises from it, it is only the latter that is of importance, for in the later stages of sperm formation, when the nucleus becomes more and more compact, the shallow cup which was seen in the early stages gradually disappears and in the fully formed sperm is not visible at all The arrangement by which, therefore, the acrosome of the ripe sperm is anchored to the nucleus is by the plug fitted into the pit and is the most effective manner in which the two are held together I am therefore inclined to believe that the formation of the shallow cup in the early stages is only a prelude to the development of the pit and that the former disappears when the latter is formed I am not aware if a similar mechanism exists and has been reported in any other animal and it will doubtless prove a useful contribution to correlate the form and size of the acrosome with the acrosome seat.

The assumption of the final form and shape of the acrosome from the original spherical vesicle is also full of interest When first formed, the vesicle is small but by the time it is planted in the cuplike depression in the nucleus it is much enlarged and very conspicuous (Figs 3-6) Gradually it elongates and assumes a broad conical shape Its internal fibre makes its first appearance in the stage shown in Fig 8, and it will be seen that a considerable reduction in the size of the acrosome has taken place by now The acrosome, which till now is included within the cell, gradually pushes out of it as the nucleus elongates From now on the definitive form and shape of the acrosome come to be established The narrowing of its base gives it a bulbous appearance and as the final form is reached, remnants of the acrosomic vesicle, unused in the fashioning of the acrosome, are seen adhering to its tip and are finally sloughed off

(c) *The nucleus*—It has been observed already that the early spermatid has a spherical nucleus exhibiting a fine granulation. With the implantation of the acrosome

and the centrioles, the nucleus gradually increases in length till the opposite ends of the now elongate nucleus are occupied by the acrosome and the centrioles respectively. The formation of the acrosome seat has already been described. The rim of the cup-like acrosome seat as well as the plug that arises from its bottom centre are deeply stained, the latter entering into the nucleus to about half its length in early stages (Figs 5-7). The nucleus continues to elongate and is seen gradually to lose some of its staining capacity till at the maximum stage of its elongation it stains faintly. The maximum length to which the nucleus grows in *Ichthyophis glutinosus* is over 16 microns. Such a spermatid is shown in Fig. 9. It will be seen that the acrosome is well placed on the nucleus anteriorly and has a broad conical outline with the central fibre in a line with the lance-shaped plug penetrating into the deep tubular acrosome seat. At its posterior aspect the nucleus shows distinctly the ring centriole (proximal centriole) stuck to it, and the granular centriole (distal centriole) with its filament has passed through the ring and has become incorporated in the nucleus.

The next change in the nucleus is the contraction in its size, both in length and in girth. The first stage in this contraction is illustrated in Fig. 10. It will be seen that the contraction begins at the posterior end of the nucleus. In the earlier stages the thickness of the nucleus is very much more than the diameter of the disc-shaped proximal centriole which therefore occupies a small area at its posterior end. Gradually the diameter of the nucleus is reduced till it is the same as that of the disc-shaped proximal centriole (Fig. 10). This nuclear contraction begins close to the centriole and gradually extends forwards till the whole nucleus assumes the shape of a deeply stained homogeneous cylindrical rod with the flat disc shaped centriole attached to its posterior end. There is a shortening in the length of the nucleus also till in the final stages of contraction the nuclear length and diameter are 8 and 2 microns respectively, while in the stage of maximum elongation the measurements were 16 and 4 microns respectively. Correlated with this shortening in length and reduction in size, there is a progressive increase in its basophily till the nucleus in the adult sperm stains very intensely with basic dyes.

At the first sign of contraction of the nucleus, which, as has been observed, begins at its posterior end, a small space appears around the contracting nucleus (Figs. 10, 27). This clear space has a definite wall which separates it from the surrounding cytoplasm and it is seen that the posterior end of the nucleus is freely suspended in it. Its size and shape lead me to believe that the space originates after the beginning of the contraction of the nucleus and has indeed been brought about as a result of it. The wall bounding the space recalls the extent of the nucleus before contraction and its size closely corresponds to the original size of the nucleus. So the conclusion appears to me inescapable that the space is formed as a result of the contraction of the nucleus and that its receding wall has left behind a delicate membrane which now bounds the space. Gradually the space becomes larger and surrounds the nucleus both posteriorly as well as on the sides. This is only to be expected as the contraction is not only in length but also in diameter so that the space is left behind by the nucleus which is shrinking in length as well as in thickness. In the stage shown in Fig. 28 the space is considerable and is found posteriorly and laterally also. It is not found anteriorly, i.e. in the acrosomal region, which points to the conclusion that the contraction in the length of the nucleus takes place only posteriorly, the anterior end, as a fixed body, drawing the posterior end into it. This is confirmed by the fact that the gradual increase in the basophily of the nucleus, referred to above, also begins at the posterior end and moves on towards the anterior end of the nucleus (Fig. 10). So the beginning of the consolidation and condensation of the nucleus is first seen at its posterior centrosomal end gradually affecting the whole nucleus in a forward movement of the process.

It has been observed that the space in question is formed in place of the nucleus during the process of contraction in size, and appears as a clear area behind and on the sides of the nucleus. The axial filament alone passes through this space into the cytoplasm behind and so out of the cell. No other contents could be made out in the cavity. That it has some kind of bounding membrane is undoubted. But how this membrane is formed and what its structure is, I cannot say. But it is not far wrong to

surmise that since originally the nuclear wall occupied this position, in the process of its contraction it has left behind a membrane. The space becomes larger and surrounds the whole nucleus except anteriorly. But later it becomes drawn out backwards and comes to occupy, mostly, the posterior region of the nucleus and lies as a clear vesicular blob behind it. Examination of this and the succeeding stages reveals very interesting facts. The space with its transparent membranous wall is pushed backwards from the sides of the nucleus (Fig 11) and in the stage illustrated in Fig 12 occurs as a tube completely and entirely post-nuclear in position and surrounding the axial filament. At this stage no trace of the space is found at the sides of the nucleus. This backward migration of the original circum-nuclear space can easily be traced to its final post-nuclear position around the axial filament.

It has already been observed (page 272) that behind the nucleus of the adult sperm is a conspicuous region consisting of a tubular sheath in which the mitochondria were arranged as a spiral investment around the axial filament. The cavity of the tubular sheath is the space we have been following so far and the wall of the sheath is the membranous wall of the space (cf Figs 13 and 21). So far as the examination of my material goes, I am convinced that the space around the nucleus seen in early stages becomes later the cylindrical tube of the 'middle piece' within which the mitochondrial investment around the axial filament is seen.

(d) *The Golgi bodies* —The Golgi bodies can be studied very well in Mann-Kopsch and Kolatchew preparations. After having taken part in the secretion of the acrosomic vesicle they travel backwards alongside the elongating nucleus. This backward movement of the Golgi bodies begins at a stage illustrated in Fig 17, and by the time the stage shown in Figs 18 and 32 is reached all the Golgi bodies have migrated posteriorly and have become grouped in the cytoplasm in that region. Towards the end of spermateliosis these Golgi elements are collected together and sloughed off in the residual protoplasm (Fig 20).

(e) *The Mitochondria* —The history of the mitochondria, on the other hand, is slightly more complex. In the spermatid they are in the form of granules scattered in the cytoplasm with a slight aggregation about the sphere. As the nucleus elongates the mitochondria move down the cell and at the stage represented in Fig 18, where the Golgi bodies have occupied a post-nuclear position, many of the mitochondrial granules have come to occupy this region. In this position the mitochondria become more closely packed around the axial filament of the tail in the form of a spiral (Figs 21, 22). This spiral disposition of the mitochondria is seen well in all osmic and chrom-osmic materials. But in Bouin preparations the mitochondria are not seen and all that one notices is the cylindrical tube of the 'middle piece' through which the filament passes (Fig 13).

The axial filament of the tail and its spiral investment of mitochondria are externally bounded by a fine transparent sheath. This sheath, which is in the form of a cylindrical tube, arising from the posterior aspect of the nucleus extends over 5-6 microns. The development of this sheath and the details of its formation I have already dealt with. The mitochondrial investment within the sheath enclosing the base of the axial filament marks the 'middle piece' of the sperm of *Ichthyophis*.

The axial filament during its passage through the middle piece is devoid of its undulating membrane and acquires it only as it leaves the tube as a free filament. It is probably developed, as in other animals, as an extension of the filament itself.

The early spermatids bound an irregular area in the deeper parts of the testis locule and as spermateliosis advances, they become more and more a compact mass of cells till finally the spermatozoa, when fully developed, arrange themselves to form a hollow hemisphere, whose wall is made up of the nuclei, whose acrosomes are directed towards the cavity of the hemisphere and whose tails are turned away from it. In this position the final stages of spermateliosis are passed through, after which the arrangement is broken up, and the sperms, about to be shed, lie scattered in groups in the substance of the locule. They later make their way into the funnel-shaped space at the mouth of the duct into which they are fed and are carried away.

## DISCUSSION.

From the above account of the spermateliosis of *Ichthyophis glutinosus* it will be clear that the problem of sperm formation in Apoda is full of interest. The adult sperm itself resembles that of the Anura and is very different from that of the Urodela. The presence of the two centrioles (proximal and distal) in close proximity of the nucleus and also of the post-nuclear mitochondrial aggregation constitute features of similarity with the anuran sperm, while absence of the characteristic modifications of the centrioles found in the Urodela clearly takes the Apodan sperm away from the Urodela. The enlargement of the proximal centriole to form the conspicuous body or the elongation of the ring-shaped distal centriole both of which are characteristic of the Urodela are absent from the Apodan sperm. The developmental history of the sperm of *Ichthyophis* lends support to this conclusion.

*The Centrioles*—The early spermatid in all Amphibia shows two centrioles, which at first are granular but which later become transformed along two different lines in the Anura and Urodela. In the Anura (Broman, 1900, 1901, 1907, King, 1907, Champy, 1913, 1923) they remain as simple granules, close to each other behind the nucleus. In *Hyla* (Retzius, 1906), however, they are separated over a short distance. In the Urodela (Meves, 1897, Macgregor, 1899, Terni, 1911, Champy, 1913, Bowen, 1928; Gatenby, 1931) one of the centrioles,—the proximal,—enlarges into a conspicuous cylindrical structure stuck to the posterior end of the nucleus (often called the 'middle piece'), while the distal centriole becomes a ring and is elongated in the form of a pessary-shaped structure running over a considerable distance along the tail. The condition of centriole modification in the Apoda as exemplified by *Ichthyophis* appears to be intermediate between these two extremes. It is neither so simple as in the Anura, nor so complicated as in the Urodela. The proximal centriole is converted into a ring (unlike the urodele, where it is the distal centriole that becomes ring-shaped) and becomes a flattened plate or disc with an orifice in the centre. This flat plate is stuck to the posterior pole of the nucleus in the same manner as the proximal centriole of the Urodela. The distal centriole, on the other hand, remains simple, and with its filament passes through the aperture of the flattened proximal centriole and enters the nucleus.

The conversion of one of the centrioles into a ring has been described in a number of Amphibia, and in all these cases the ring is formed *before* the centrioles come in contact with the nucleus. It is common, therefore, to see in the cytoplasm of the developing spermatid, the two centrioles free in the cytoplasm, one of them in the form of a ring. The attachment of the centriole (or centrioles) with the nucleus takes place afterwards. In this respect, *Ichthyophis* differs from the other Amphibia. In this animal, and probably in other Apoda also, the ring centriole is never seen free in the cytoplasm and the conversion of the proximal centriole into a disc-shaped ring takes place only *after* its attachment with the nucleus and never before. Pictures, therefore, similar to those in other Amphibia, where the ring is free in the cytoplasm are never met with in *Ichthyophis*.

Broman (1907) has noticed in *Rana fusca* that when the centrioles migrate deeper towards the nucleus from the periphery, the cell membrane also becomes indented, so that the distal centriole with its filament lies at the bottom of a pit-shaped depression and that therefore the filament preserves the same extra-cellular position and nature as it did before, when the distal centriole was at the periphery. This does not occur in *Ichthyophis* and I have not seen a depression of the cell wall following the inward migration of the distal centriole. If this difference means anything at all, it means that the relation between the distal centriole and the cell membrane is far more intimate in *Rana fusca* than it is in *Ichthyophis* and many Urodela and Anura, where also the distal centriole along with its filament simply moves through the cytoplasm towards the nucleus.

*The Acrosome*—That the acrosome is the product of the Golgi apparatus of the spermatid is well known but the details of its formation and also its relationship with the nucleus are not clearly understood. The form, size and shape of the acrosome are subject to great variation among animals and the manner of its formation and the mechanism by which it is fitted on to the nucleus become matters of great interest. The

reason for the lack of our knowledge of this aspect of sperm-formation is due, partly as Gatenby (1931) suggests, to the fact that the development of the acrosome is screened by the large acroblasts, and partly also to the relatively greater attention paid to the changes in the posterior part of the nucleus (because the centrioles occur in this region) rather than to the anterior

It has already been observed that the acrosome in *Ichthyophis* is incorporated with the nucleus of the growing spermatid with reference to an acrosome seat. The only other case of an amphibian where an acrosome seat has been described is that of the urodele, *Desmognathus*, where the details of the association between the nucleus and the acrosome have been described by Gatenby (1931). This author finds in the spermatid of *Desmognathus* a number of granules in the neighbourhood of the forming acrosome, which eventually 'close up together and form an acrosome seat'. Into this seat, which is in the form of a shallow cup in the nucleus, the acrosome is later fitted. The acrosome seat is, therefore, a new structure described by Gatenby for the first time in vertebrates. But granules similar to those which Gatenby describes had been reported earlier by Meves (1897) in the salamander, by MacGregor (1899) in *Amphiuma*, by Terni (1914) in *Geotriton* and by Bowen (1922) in *Plethodon*. But none of these authors had followed the fate of these granules or determined their significance and it is Gatenby who has studied their real nature and has associated them with the formation of the acrosome seat.

It must be emphasised that an acrosome seat can clearly be made out in the developing spermatozoon of *Ichthyophis glutinosus* and though I am unable to detect any granules that give rise to it, the presence of an acrosome seat is beyond doubt. It forms a conspicuous organ of the developing spermatid. In fact, it is much clearer than in the urodele spermatid. Unfortunately, Gatenby has neither figured nor described the later appearance of the acrosome seat in *Desmognathus* or any other urodele. In this respect, therefore, my study of the acrosome in *Ichthyophis* is an extension of that of Gatenby and I might mention here that the problem of the acrosome seat and its formation is a fruitful field of study, not only in vertebrates but in invertebrates also seeing that the acrosome, of all things, is the most variable in the sperms of animals.

The details of the formation of the acrosome seat have been described earlier. That it is formed in a manner different from that in *Desmognathus* as described by Gatenby is clear. In *Desmognathus* a number of granules are found around the acrosome and these run together and form the acrosome seat. It is at this stage that Bowen (1922) saw the granules in *Plethodon* though it was not clear to him what purpose these granules served. They are said to be best preserved in preparations made from acetic-free fixatives, though Gatenby himself has seen them in Flemming-acetic fixed material. The details of the manner in which these granules 'close up together' to form the acrosome seat have not been described either by Gatenby or by any other worker. Had they been, they would have constituted a very interesting chapter in spermatogenesis.

In *Ichthyophis* I have not seen in any stage of spermatogenesis, the granules that Gatenby, Bowen and others have described. Since reading Gatenby's paper, I have diligently looked for them in material prepared in a variety of ways,—in preparations made from acetic-free fixatives, in Da Fano-haematoxylin preparations, in chrome-osmic preparations and in Flemming material with and without acetic acid, but have not found them. The variety of treatment that my material has received is so great that if the granules were present they would have turned up in one or the other of my slides. Bowen's figures of *Plethodon* spermatids (Cajal-gold chloride-haematoxylin preparations) indicate that the granules are numerous and of large size, and these figures as well as those of Gatenby would have enabled me to identify the granules, were they present. I am, therefore, convinced that these granules are not present in *Ichthyophis* spermatids in any stage of acrosome formation.

The further history of the acrosome seat, the final form it takes and the manner in which the ultimate relationship between the acrosome and nucleus is established in the ripe spermatozoon have already been described at length, and in the absence of previous studies on the subject, I am able to say no more at present than that future work will

throw more light on this interesting problem of the association between the acrosome and nucleus in the flagellate sperm

*The Nucleus*—Two facts emerge from a study of the changes undergone by the nucleus during spermateliosis. The first relates to the change in its form, size and shape, the second concerns the space that appears round the nucleus in later stages. I shall deal with these two separately.

The spermatid nucleus is spherical, and as spermateliosis is initiated it becomes an elongated cylinder which grows in length gradually till a maximum is reached (Fig. 9). After this maximum point in elongation is reached, the nucleus starts shrinking in size, both in length and in girth, till the final compact cylindrical homogeneous rod which is the nucleus of the adult sperm is reached (Fig. 13). The condensation and consolidation of the nucleus begins posteriorly and extends forwards as illustrated in Figs. 10, 27 and 28, till the whole nucleus is affected by it. The change from the spherical spermatid nucleus of the early spermatid into the cylindrical rod-like nucleus of the adult sperm is, therefore, one of the fundamental factors in spermateliosis. In this change there is also a reduction in volume of the nucleus. It is generally understood that the nucleus of the adult sperm is a highly concentrated mass of chromatin where no non-essential element is included while the nucleus of the spermatid has, besides chromatin, other materials, of which fluid is an important constituent. In the change from the spherical spermatid nucleus to the cylindrical rod nucleus of the spermatozoon is also involved a process of considerable reduction in volume. The exact relationships between the volume of the spermatid nucleus and of the spermatozoon I have reserved for a future communication where I hope to deal with the precise nature and extent of these volume changes in the different examples of Apoda.

The second point of interest that relates to the nucleus is the space that appears around it, especially posteriorly, as the nucleus contracts. It has been observed that as the nucleus, after it reaches its maximum elongation, commences to contract, a space appears around the contracting nucleus, at first posteriorly, and later on the sides also. This space appears to have a definite wall, and, gradually moving backwards, assumes a post-nuclear position in the form of a cylindrical tube. This tube is the sheath of the 'middle piece' of the sperm of *Ichthyophis*.

A space around the nucleus during spermateliosis has only been studied by Gatenby (1931) in *Desmognathus*, but he neither accounts for its origin nor does he trace its fate. He finds the space on the sides of the nucleus and not posteriorly. No other account of this space is found in literature, so far as I am aware, and my conclusions regarding the space as the fore-runner of the tube of the 'middle piece' mark the first attempt at accounting for the origin and tracing the fate of this structure.

There is, however, one apparent difficulty in accepting this interpretation. The space, as we have seen, is originally formed as a clear vesicular cavity separate from the cytoplasm and remains so for a considerable period of its existence. The question arises,—how then have the mitochondria which are in the cytoplasm and *outside* the space, come to be included *inside* it in the final stages? It will be seen that the extent of this difficulty depends on the importance attached to the closed nature of this space. For, if it is a cavity completely cut off from the cytoplasm throughout its existence, then obviously the presence in it of no cytoplasmic material can be explained. But then no such space is seen in the later stages, either behind the nucleus or surrounding it. In fact, the presence of this clear transparent vesicle is as characteristic of the early stages as its absence is of later ones. On the other hand, it is not impossible that this space is, even from the beginning, open posteriorly. There are two reasons for this possibility. First, if the wall of the space is caused, as it has been assumed, by the shrinking of the nucleus, then necessarily it is incomplete posteriorly; for here, there is no nuclear wall but the broad disc-like proximal centriole. Secondly, from the very start there is bound to be an orifice, or at least an incompleteness in the wall, for the passage of the axial filament. It is precisely at this posterior position that the wall is absent in the adult sperm. The sheath is like an open cylindrical tube, one end of which is stuck to the nucleus, while the other, the posterior end, is free and open. I believe that it is at this

open posterior end of the elongating sheath which is coming to occupy the post-nuclear position that the mitochondria move up and arrange themselves in a spiral fashion. No other explanation appears possible. No other organ could possibly give rise to the tubular sheath of the 'middle piece' and no other organ could have originated from the circum-nuclear space and its wall.

To my knowledge this is the first time an attempt to account for the tubular sheath of the 'middle piece' of the sperm and to correlate it with the circumnuclear space is made. The need to distinguish between the mitochondrial spiral and the tubular sheath that invests it is clear, and while the earlier studies on Amphibian spermateliosis contained merely the observation that the mitochondria aggregate around the base of the axial filament, here is offered for the first time an intimate and detailed picture of the structure of the 'middle piece' and an effort has been made to explain and interpret it.

*The Golgi Apparatus*—The only function of the Golgi apparatus in the spermateliosis of *Ichthyophis glutinosus* appears to be the secretion of the acrosome. After that is done, the discrete Golgi elements, into which the original more compact structure breaks up, move backwards and are collected in the residual cytoplasm to be thrown away. Gatenby (1931) on the other hand sees a significance in the backward migration of the Golgi bodies. In the urodeles he has studied, he thinks it possible that the Golgi bodies, after reaching the post-nuclear region contribute in some manner to the formation of the clear space found behind the post-nuclear plate in these animals. This space is further supposed to contain a fluid contributed by the idiozome. The post-nuclear space has been noticed earlier by Macgregor (1899) in *Amphiuma* but he has accounted for its origin from the remnants of the sphere, which according to him, migrates backwards to the post-nuclear region. In *Ichthyophis* neither the post-nuclear plate nor the clear vesicle is seen and I have at the moment no means of explaining the backward movement of the Golgi bodies except to be sloughed off (Fig. 20). The question of the persistence of the Golgi bodies in the adult spermatozoon has been raised by Gatenby (1931) who, following Turni (1922,) is not sure that they are not present in the ripe sperm. I have not used any special methods for the detection of the Golgi bodies in the fully formed ripe sperm, but from the examination of sections and smears prepared in a variety of ways, I have not seen them in the ripe sperm and it can be stated with a fair amount of certainty that all the Golgi bodies are thrown away in the scaled off protoplasm. It therefore means that while in the Urodela, the Golgi-idiozome complex has a dual function, i.e. that of producing the acrosome in front of the nucleus and the post-nuclear vesicle behind it, in *Ichthyophis*, as in the majority of animals, it has a single function,—the formation of the acrosome.

*The Mitochondria and the 'middle piece'*—The interest attached to the mitochondria lies in the fact that they persist in the adult sperm. They are arranged in the form of a spiral aggregation around the axial filament behind the nucleus to constitute the 'middle piece' of the sperm of *Ichthyophis*. In this animal, therefore, the 'middle piece' is a mitochondrial one and so far as the centrioles are concerned, is entirely posterior to both of them.

The term 'middle piece' is used more for convenient usage than for designating a particular structure of the sperm, and a review of the constitution of the sperms of different animals shows that the term is used to denote a part of the sperm showing great variation in structure. The 'middle piece' of an insect sperm is quite different from the molluscan, anuran, urodelan or mammalian sperm. In the insect, the short region behind the nucleus where the two centrioles are lodged, is termed the 'middle piece' while the mitochondrial investment of the tail, which is of considerable length, is not reckoned in this definition. In the mammal, the two centrioles (or the products of their division) are separated by a shorter or longer distance along the sperm behind the head and this region, whether associated with mitochondria or not, is called the 'middle piece', the extent between the two centrioles being used as a criterion of consideration. In the anurous amphibian, the two centrioles are lodged close together behind the nucleus but the mitochondria invest the axial filament behind the centrioles over a short distance, this part being called the 'middle piece'. In the 'middle piece' of the anuran, there is no part of the centriolar apparatus included. The centrioles are placed close together in the neck and the 'middle

piece', which is purely mitochondrial, is posterior to it. In *Hyla* however, Retzius (1906) has noticed a spacing of the centrioles, which are placed one behind the other, with a gap between them, marking off a 'middle piece' in the true mammalian sense of the term. Lastly, in the urodele sperm which is one of the most unique in animals, following the head is a very large and elongate proximal centriole which is called 'middle piece' and behind it the distal centriole is drawn out over a considerable distance as a greatly elongate pessary shaped structure. From this it is clear that the term 'middle piece' is a vague and loosely applied one denoting a more or less clearly differentiated part of the sperm that follows the nucleus, irrespective of its constitution or structure and it will be seen that while in some, the centrioles and their extensions mark the 'middle piece', in others, the mitochondria do.

In this respect, a comparison of the Apodan sperm as exemplified by that of *Ichthyophis* with the types described above, is very interesting. As already observed, both the centrioles are closely applied to the nucleus, one as a flat plate with a central perforation through which the other, in the form of an elongated spindle shaped granule penetrates and is sunk in the nucleus. No part of the centriolar apparatus is found behind and free from the nucleus in the sperm of *Ichthyophis*. The 'middle piece' of this sperm is merely the base of the filament enveloped by the spiral mitochondrial investment enclosed in its sheath. It extends over 5 to 6 microns and is the only conspicuous portion of the sperm behind the nucleus. Behind it the axial filament is free as a long vibratile flagellum and is provided over a greater part of its length with an undulating membrane. The 'middle piece' of the sperm of *Ichthyophis* resembles that of the anuran sperm where also it is mitochondrial and not centrosomal.

#### SUMMARY

The acrosome of *Ichthyophis glutinosus* is a bulbous body and is attached to the nucleus of the sperm in connection with an acrosome seat consisting of a lance-shaped plug from the acrosome which fits into a deep pit in the nucleus.

Both the centrioles are lodged behind the nucleus, the proximal ring centriole is applied to the nucleus posteriorly as a flat disc with an orifice in the centre, through which the distal centriole carrying the filament, is stuck in the nucleus.

The 'middle piece' consists of a spiral disposition of mitochondrial granules around the base of the axial filament, lodged in a tubular sheath. It is purely a mitochondrial 'middle piece', there being no part of the centriolar apparatus included in it.

The tubular sheath of the 'middle piece' is formed from the space that arises posterior and lateral to the nucleus as the latter shrinks in size during the later stages of spermatogenesis. The mitochondria migrate into it later.

The Golgi-ridosome complex, after the secretion of the acrosome, breaks up into distinct Golgi bodies, which travel backwards and are discarded with the sloughed off protoplasm.

The axial filament carries an undulating membrane over the greater part of its free length.

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### EXPLANATION OF PLATE III

- Fig 25.—Photomicrograph of early spermatids of *Ichthyophis glutinosus* showing the acrosomic vesicle, acrosome seat and the posterior centrioles. The filament also is seen.  $\times ca$  733
- Fig 26.—Later spermatids illustrating closer incorporation of the centrioles with the nucleus. The ring centriole is stuck posteriorly while the spindle-shaped distal centriole, passing through the ring has entered the nucleus.  $\times ca$ . 733
- Fig 27.—Later stage in spermatogenesis. The nucleus has elongated and has become narrower. The contraction of the nucleus has begun posteriorly and the space around the contracting end has made its appearance.  $\times ca$  733
- Fig 28.—The contraction is more pronounced here and makes the posterior part of the nucleus look much darker and more deeply stained than the anterior. The space around the posterior end is clear. The plug like acrosome seat is also seen.  $\times ca$ . 733
- Fig 29.—Later stage. Closer examination shows the disc-like centriole stuck to the nucleus posteriorly as a plate and a non-staining area separates the two.  $\times ca$ . 733.
- Fig 30.—Photograph showing the form of the acrosome in the fully formed sperm.  $\times ca$  733
- Fig 31.—Early spermatid showing the acrosomic vesicle at one pole of the nucleus and the Golgi bodies around the vesicle. The plug like beginning of the acrosome seat is also seen. The mitochondria are granular.  $\times ca$ . 1466
- Fig. 32.—Later stage of spermatid showing the Golgi bodies aggregated posteriorly. The detailed structure of the acrosome seat is clear.  $\times ca$  733
- Fig 33.—The anterior end of a fully formed sperm of *Ichthyophis glutinosus* showing the nucleus, the acrosome, acrosome seat and the mitochondrial middle piece.  $\times ca$ . 2200.



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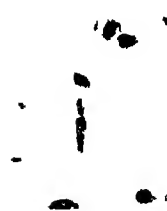
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# ON THE RAMAN SPECTRA OF A FEW ALKYL SULPHIDES IN THE SOLID STATE

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## ABSTRACT

The Raman spectra of methyl, ethyl, propyl and butyl sulphide have been studied in the liquid state and in the solid state at the temperature of liquid oxygen. The polarisation of the lines in the liquid state has also been studied in the present investigation. Disappearance of some prominent Raman lines and changes in the relative intensities of the lines with the solidification of the substance have been observed in each case. The causes of these changes have been discussed and the changes have been correlated in the cases of methyl, ethyl and propyl sulphide to strong association of the molecules in the solid state through hydrogen bond in the first case and probably through a sulphur bond in the other two cases. In the case of butyl sulphide the disappearance of the lines is attributed to the absence of free rotation about the C-C bond in the solid state.

## INTRODUCTION

The Raman spectra of a large number of organic compounds have been investigated in the solid state at low temperatures by many workers previously. It was first observed by Gross and Vuks (1935) that in the case of some aromatic compounds some new Raman lines appear in the low frequency region when the substances are solidified. The origin of the lines was attributed to lattice oscillations. Such intense new lines were also observed later by Sirkar (1936) in the case of simple centro-symmetric molecules such as  $\text{CS}_2$ , naphthalene and *p*-dichlorobenzene and it was pointed out by him (Sirkar, 1937) that in the case of naphthalene and *p*-dichlorobenzene large changes in the polarisabilities cannot be produced by intermolecular oscillations in the unit cell of the crystal. Although a different hypothesis has been put forward (Venkateswaran, 1938) regarding the nature of these lattice oscillations, the large intensities of the new lines observed in the case of centro-symmetrical crystals cannot be accounted for by such a hypothesis.

A second type of change in the Raman spectra was observed by Mizushima *et al* (1936) in the case of a few organic compounds when these substances were solidified. In the liquid state each of these substances gives a large number of Raman lines, but when it is solidified some of the prominent lines disappear. This fact has been explained by the said authors on the assumption that owing to free rotation about single bonds the liquid state contains two types of molecules, one of the *trans* form and the other either of the *cis* or of the *gauche* form, and in the solid state the molecules exist only in one of these forms. It is true that this hypothesis can explain the number of lines observed in the case of a few substances in the solid state quite satisfactorily, but from a closer examination of the results reported by the said authors in the case of a few other substances it appears that all the lines observed in the liquid and solid states cannot be accounted for by such a hypothesis. The free rotation about the single bond might exist in many other aliphatic compounds and it would be of interest to investigate whether the Raman spectra undergo any such changes as observed by Mizushima *et al* (1936) when these substances are solidified and whether the hypothesis put forward by them can account for all the lines observed in these cases. Also from a comparison of the Raman spectra of a large number of aliphatic and aromatic compounds in the solid state with those for the liquid state, it might be possible to obtain some information regarding the general laws which govern the intensities of the new lines appearing in the low frequency region in the solid state. With this object in view investigations on the Raman spectra of aliphatic and aromatic compounds in the solid and liquid states have been undertaken.

and the results obtained for methyl, ethyl, propyl and butyl sulphide are discussed in the present paper

### EXPERIMENTAL

The investigation of Raman spectra in the solid state of substances which are in the liquid state at the room temperature is beset with the difficulty that if the liquid is solidified by immersing the glass tube containing it in a refrigerant such as liquid oxygen, a translucent white mass is obtained in most cases. Stray light is so intense in comparison with the light scattered by molecules in these cases that it is difficult to get the Raman lines photographed with any clear background. To overcome this difficulty, Mizushima *et al.* (1938) used a liquid bath which was cooled by immersion in liquid oxygen, so that the solid mass obtained was sufficiently transparent. In the present investigation a slightly different method has been used so that the substances having freezing points, which are slightly higher than the boiling point of liquid oxygen, as well as those solidifying at temperatures only a few degrees below the freezing point of water, can be investigated with this arrangement.

The liquid distilled in vacuum is put in a double walled cylindrical vessel, and in order to evacuate the volume between the two walls a side tube is connected through a stop-cock to a pumping system. Dry air can be introduced at any desired pressure through another stop-cock connected to the side tube. When initially the double-walled vessel is inserted in liquid oxygen contained in a larger Dewar vessel, the pressure inside the annular space between the two walls is made very low and so the rate of cooling of the liquid becomes very slow. When the substance is solidified, the pressure inside the annular space is raised slowly by introducing small quantities of dry air through the second stop-cock mentioned above and finally the pressure is made equal to the atmospheric pressure so that the temperature of the substance approaches very nearly that of the liquid oxygen. Suitable portions of the outer Dewar vessel are blackened and the substance is illuminated with the two vertical quartz mercury arcs, the light being focussed with the help of two six-inch glass condensers. The scattered light emerges through a window on one side. A short glass tube provided with a side tube is attached to the outer Dewar vessel against the window with sealing wax and its mouth is closed by a glass plate attached with sealing wax. The side tube is connected to a pump and the tube is evacuated. This prevents the moisture from being deposited on the window. It was observed in the preliminary tests that in the case of any liquid the solid mass, obtained with the help of this apparatus, was much more transparent than that obtained by immersing an ordinary pyrex tube containing the liquid in liquid oxygen.

A Fuess spectrograph having optical parts of glass was used in the present investigation. It has a dispersion of about 14 Å U per mm in the region of 4046 Å U. A blue glass filter was placed in the path of the incident light in order to diminish the intensity of the continuous background in the region on the long wave-length side of 4500 Å U and to cut off the line 5460 Å U. The polarisation of the Raman lines due to the liquid state was studied in each case by photographing simultaneously spectra of the vertical and horizontal components of the scattered light with the help of a double image prism. Light from a mercury arc focussed with the help of a condenser was used as the incident light in this case also. The spectrograms, therefore, only indicated whether any Raman line was partially polarised or completely depolarised and no attempt has been made to measure the absolute values of factor of depolarisation accurately.

### RESULTS AND DISCUSSION

The results obtained for methyl sulphide are given in Table I. The Raman spectrum of the liquid was studied previously by Venkateswaran (1931), Kohlrausch (1936) and Medard *et al.* (1936). There were some discrepancies in the results reported by these authors and so Fonteyne (1940), while studying the infra-red absorption spectrum of methyl sulphide investigated the Raman spectrum and also the polarisation of the Raman lines. His results were compared by him with those of previous workers. The results given by

Fonteyne are included in Table I for comparison. Some weak lines reported by him are not observed in the well-exposed spectrogram due to methyl sulphide obtained in the present investigation

TABLE I  
*Methyl sulphide*

Liquid at room temp		Solid state at about $-180^{\circ}\text{C}$ (Present authors)
Fonteyne	Present authors	
285 (s, P)	282 (2d), e $\rho > 0.6$	70 (1), k
480 (vw)	$< 6/7$	84 (1), k
690 (vs, P)	693 (8s) k, e P	338 (1), e
742 (s, D)	740 (3d) k, e D	402 (0), e
910 (vwb)		691 (3s) k, e
1041 (vw)		740 (2s) k, e
1224 (vw)	1335 (0d) k	
1325 (w, P)	1424 (2) k, e D	
1426 (mb, D)	1440 (1) k, e D	1450 (1s) k, e
1609 (vw)	2832 (2) k, e P	
2832 (w, P)	2852 (1) k, e P	
2911 (vs P)	2915 (10s) k, e P	2915 (2d) k, e
2980 (s b, D)	2990 (5d) k, e D	2970 (2dd), k, e

In this table and in the following tables the intensities are given in parentheses. The letters s, b and d signify sharp, broad and diffuse respectively. The letters k, e and  $\rho$  represent exciting lines in Kohlrausch's notation. P means  $\rho < 6/7$  and D means  $\rho = 6/7$ .

The results given in Table I differ slightly from those reported earlier (Sirkar and Bishui, 1943) in this respect that a line 1440 has been observed later to be just resolved from the stronger line 1424 and the polarisation of the line 282 has been given more precisely. Formerly it was given as  $\rho \sim 6/7$ . According to Fonteyne this line is well polarised. Actually, however, the value of  $\rho$  is greater than 0.6 and less than 6/7.

In the solid state the line 282 is not observed, but two new lines 338(1) and 402(0) appear in its place. The line 1440 becomes stronger and shifts to 1450 while the line 1424 which is stronger for the liquid state becomes too weak to be observed and two new lines 70 and 84 appear in the solid state. Fonteyne (1940) assumed that the molecule of methyl sulphide possesses the symmetry of the group  $C_{2v}$  and showed that it has 21 fundamental modes of vibration. He also made assignments of some of these vibrations to the Raman lines observed. Thompson (1941) more recently studied the infra-red spectrum of this substance and revised some of the assignments made by Fonteyne. According to both of them the line 282 is due to the C-S-C deformation oscillation. According to Thompson the line 1424 is due to the  $\text{CH}_3$  bending oscillation symmetric to the plane of C-S-C and the line 1440 to similar vibration either totally symmetric or anti-symmetric to  $\sigma_v$  and  $\sigma_v$  and symmetric to the twofold axis. The assignment of the latter line was not definite because its polarisation was not given by Fonteyne. This line is now observed to be depolarised and so it should be identified with  $\nu_2$  given by Thompson. Thus the frequencies of the C-S-C and  $\text{CH}_3$  bending oscillations are observed to undergo changes with the solidification of the substance. There is also marked change in the relative intensities of some of the lines with the solidification. For instance, in the liquid state the line 2915 (k) is more intense than the line 693 (k, e), but in the solid state the intensity ratio is reversed. This change cannot be due to the absorption of the line 2915 in the solid state owing to its high degree of polarisation, because the line 693 is also

highly polarised and its intensity would also be reduced in the same proportion had such absorption taken place in the crystal. On the other hand, such a change in the relative intensities of the lines might be due to the presence of strong association of the molecules in the solid state through the hydrogen bond. This view is corroborated by the fact that the line 1426 due to the bending  $\text{CH}_3$  oscillation symmetrical to  $\sigma_v$  is weakened very much in the solid state. It appears from these results that the plane of symmetry through the  $\angle \text{CSC}$  angle is probably not present in the solid state as far as the hydrogen atoms are concerned. The angle  $\angle \text{CSC}$  probably does not change with the solidification, because the lines 693 and 740 due to CS valence oscillations do not shift appreciably. The origin of the lines 70 and 84 might be traced to the intermolecular oscillations and the strong association through the hydrogen bonds mentioned above may be responsible for their appearance.

### Ethyl sulphide

The results for ethyl sulphide are given in Table II. These have been collected from a good spectrogram obtained recently after repeated trials. The polarisation of the lines given in Table II are those obtained in the present investigation. No such data were reported by previous workers. The Raman spectrum of this substance was studied previously by Venkateswaran (1931), Meyer (1931), Matossi *et al* (1931) and Thatte and Ganesan (1933). The lines reported by these authors are all given in Table II. No special attempt has been made in the present investigation to record the very faint lines for the liquid, because it was found impossible to detect such lines in the case of the solid state owing to the presence of unavoidable stray light. Table II shows that the lines 640 and 657, which are prominent in the liquid state, disappear in the solid state, although the neighbouring line 690 is quite intense in the solid state. If it is assumed that the  $\angle \text{CSC}$  angle is less than  $180^\circ$ , the line 690 may be ascribed to the  $\angle \text{CSC}$  antisymmetric oscillation,

TABLE II  
Ethyl sulphide

Liquid at room temp		Solid at ca. $-180^\circ\text{C}$ (Present authors)
Previous authors	Present authors	
302 (0)	302 (0) $\sigma_v$ , P	88 (3d) $k$
336 (0)	336 (0) $\sigma_v$ , P	340 (1a) $k$
391 (0)	391 (0) $\sigma_v$ , P	
640 (3)	640 (2) $k, \sigma_v$ , P	v
657 (3)	657 (2) $k, \sigma_v$ , P	v
693 (3)	690 (2) $k, \sigma_v$ , $\rho > 6$	690 (3a) $k, \sigma_v$
790 (odd)		
976 (2)	976 (1) $k, \sigma_v$ , P	973 (1a) $k, \sigma_v$
1020 (0)		
1050 (0)	1048 (0) $k, \sigma_v$ , P	
1070 (0)	1070 (0) $k, \sigma_v$ , P	
1256 (0d)		
1333 —		
1426 (1d)	1426 (2) $k, \sigma_v$ , D	1426 (1d) $k, \sigma_v$
1456 (8d)	1456 (2) $k, \sigma_v$ , D	1456 (1d) $k, \sigma_v$
2874 (3)	2874 (2) $k, \sigma_v$ , P	2874 (2d) $k, \sigma_v$
2912 (0)		
2930 (8)	2930 (6) $k, \sigma_v$ , P	2930 (4d) $k, \sigma_v, \rho$
2970 (2)	2970 (3) $k, \sigma_v$ , D	2970 (2) $k, \sigma_v$
3010 —		

although the value of  $\rho$  appears to be less than 6/7, because there is no other depolarised line in this region. The line 640 would in that case represent the symmetric C-S valence oscillation. The disappearance of the two lines 640 and 657 is probably due to a change

in the  $\angle \text{CSC}$  angle in the solid state. In this case the  $\text{CH}_3$  groups do not undergo any change on solidification, because the corresponding lines do not undergo any change in intensity or in frequency with solidification. The hypothesis put forward by Mizushima *et al.* that the disappearance of such prominent lines in the solid state is due in many cases to the absence of free rotation about the C-C bond cannot explain the disappearance of the line due to C-S valence oscillation in the present case. The line 88 is due to some intermolecular oscillation and the association in this case is not through the hydrogen bond, but is probably through the sulphur bond.

TABLE III  
*Propyl sulphide*

Liquid at room temp		Solid at ca $-180^\circ\text{C}$ (Present authors)
Previous authors	Present authors	
146 (1)		96 (3b) k
282 (2)	282 (2) c, P	142 (1a) c
380 (1)	378 (0b) e, P	160 (1s) e
433 (0)	432 (0) e, ?	272 (2b) e
650 (4)	650 (4b) k, e, P	v
712 (2)		725 (1) k, e
734 (4)	735 (3) k, e, D	735 (1) k, e
788 (3)	787 (1) k, e, P	
850 (3)	845 (1) k, e, P	
893 (5)	892 (3) k, e, P	892 (1) k, e
1032 (8)	1032 (5) k, e, P	1032 (2) k, e
1054 (0)		
1085 (1)	1088 (1) k, e, P	
1293 (3)	1295 (2) L, D	
1329 (2)	1326 (1) k; P	
1418 (4)	1420 (3) k, e, D	1420 (0a) k, e
1450 (2)	1452 (4) k, e, D	1452 (0a) k, e
2865 (8)	2868 (8) k, e, P	2862 (3a) k, e
2902 (10)	2907 (10) k, e, P	2910 (5a) k, t, e
2927 (10)	2930 (10) k, e, P	2920 (5a) k, t, e
2965 (8)	2965 (8) k, e, D	2965 (2b) k, e

*Propyl sulphide.*

The results for propyl sulphide are given in Table III. In this case as well as in the case of butyl sulphide only those lines for the liquid state which appeared with appreciable intensity have been entered in the tables and no attempt has been made to record the extremely feeble lines recorded by previous workers. It will be observed that in the liquid state there are three lines 282 (P), 650 (P) and 736 (D), which probably correspond respectively to the deformation, symmetric valence and antisymmetric valence oscillations

of the  $\angle \text{CSC}$  group. In the solid state the line 650 disappears completely and the line 735 is split up into two lines 725 and 735 of the same intensity. Thus in this case also as in the case of ethyl sulphide there is some distortion of the molecule so as to restrict the symmetric C-S oscillation. The lines 892 and 1032 due probably to C-C valence oscillations appear in the solid state. There is a small diminution in the frequency 2930 of the C-H

valence oscillation in the solid state. Again, although the spectrogram due to the liquid did not indicate the presence of the line 146 reported previously by Venkateswaran (1931) but not recorded by Thatte and Ganesan (1933), the spectrogram due to the solid indicated the presence of two lines 142 and 160. A band at 96 was also observed but the corresponding anti-Stokes line was not observed by the side of  $\lambda$  4046. These facts show that the molecule of propyl sulphide undergoes structural changes on solidification. The free rotation about C-C bond in the liquid state cannot account for the results in this case also. It might be possible that some association of the molecules takes place through the sulphur atom in the solid state.

TABLE IV  
*Butyl sulphide*

Liquid at room temp		Solid at ca. $-180^{\circ}\text{C}$ (Present authors)
Previous authors	Present authors	
142 (0)		50 (1) <i>k</i>
274 (0)		72 (1) <i>k</i>
573 (0)	274 (0b) <i>e</i> , P	223 (1) <i>e</i>
655 (3)	331 (0b) <i>e</i> , P	
677 (0)	652 (2b) <i>k</i> , <i>e</i> , P	652 (1) <i>k</i> , <i>e</i>
715 (0)		
727 (0)		
753 (1d)	755 (1b) <i>k</i> , <i>e</i> , $\rho > 6$ $< 6/7$	755 (1) <i>k</i> , <i>e</i>
794 (1d)	795 (1b) <i>k</i> , <i>e</i> , P	
867 (3)	870 (2) <i>k</i> , <i>e</i> ; D	
892 (3)	892 (2) <i>k</i> , <i>e</i> , D	906 (1) <i>k</i> , <i>e</i>
968 (1)		
1001 (1)		
1054 (4)	1050 (3) <i>k</i> , <i>e</i> , D	1050 (1) <i>k</i> , <i>e</i>
1102 (3)	1106 (1) <i>k</i> , P	
1298 (3)	1294 (3d) <i>k</i> , D	1294 (1) $\lambda$
1331 (1)		
1417 (4)	1420 (1) <i>k</i> , <i>e</i> , D	
1454 (6d)	1454 (5d) <i>k</i> , <i>e</i> , D	1454 (2s) <i>k</i> , <i>e</i>
2873 (5)	2864 (6) <i>k</i> , <i>e</i> , P	2868 (2s) <i>k</i> , <i>e</i>
2914 (8)	2903 (10) <i>k</i> , <i>e</i> , P	2898 (3s) <i>k</i> , <i>e</i>
2934 (5)	2935 (5) <i>k</i> , <i>e</i> , P	2935 (1s) <i>k</i>
2960 (5)	2962 (5) <i>k</i> , <i>e</i> , D	2950 (1s) <i>k</i>

*Butyl sulphide*

The results for butyl sulphide are given in Table IV. The Raman scattering due to this substance is quite feeble and so the faint lines have not been recorded in the solid state. There are a large number of lines in this case and any attempt at the interpretation of the result will be a mere guess work. However, the lines 223, 652 and 755 observed in the solid state may be due to the vibrations of the CSC group as in the case of propyl sulphide. The lines 870 and 892 and 1106 which are more intense in the liquid state than the line 753 are absent in the spectrogram due to the solid. This may be due to the absence of free rotation in the solid state because these lines are most probably due to the

C-C oscillations. Thus in this case in the solid state the CSC angle remains intact and the molecule assumes one of a few configurations produced by free rotation about C-C bonds in the liquid state. The lines 50 and 72 are due to intermolecular oscillations but no direct evidence for strong association of the molecules is obtained from the results given in Table IV. The CH frequencies undergo only minor changes, but the intensities of the lines 2915 and 2950 appear to diminish with the solidification of the substance.

The Raman spectra of ethers will be analogous to those of the thioethers mentioned above and so the Raman spectra of a few ethers will be studied in order to elucidate the points mentioned above more clearly.

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# SPECIFIC IONISATION OF COSMIC RAY PARTICLES

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## ABSTRACT

An account of the cloud chamber investigation of the variation of total ionisation with energy for electrons, mesons and protons is given. The predicted relativistic rise of ionisation with energy when the kinetic energy is above the rest energy of the particle has been verified for electrons up to  $5 \times 10^8$  e.v. For mesons there is an indication of the rise in ionisation with energy, but the amount of increase is lower than that predicted by the theory. Altogether 8 protons were observed in 5,000 photographs. Their specific ionisation is in satisfactory agreement with the theory.

## INTRODUCTION

According to Bloch (1933), Bhabha (1938) and others, the total ionisation produced by a charged particle per cm. of its path is given by —

$$-\frac{dE}{dx} = 2\pi N Z r_0^2 \frac{mc^2}{\beta^2} \left[ \log \frac{mc^2 \beta^2 W_m}{(1-\beta^2) I^2 Z^2} + (1-\beta^2) \right]$$

Here  $N$  = No. of atoms per c.c. of the medium

$Z$  = atomic number,  $I(Z)$  = mean ionisation potential of the atom. Bloch put  $I = 13.5$  e.v.

$m$  = mass of the electron,  $\beta = \frac{v}{c}$ ,  $r_0 = \frac{e^2}{mc^2}$

$M, E$  = mass and total energy respectively of the charged particle

$$\gamma = \frac{E}{Mc^2}$$

$W_m$  = Maximum energy transferred to a secondary electron initially at rest

According to Bhabha (1938)

$$W_m = \frac{2mM^2C^2(\gamma^2-1)}{m^2+M^2+2mM\gamma}$$

Up to this time, this formula has not been experimentally verified over a wide range of energy of particles excepting by Corson and Brode (1938) who carried out measurements of total ionisation of Cosmic ray electrons lying within the energy range  $1 \times 10^6$  e.v. and  $3 \times 10^7$  e.v. by counting droplets on photographs taken with a counter controlled chamber. Their investigation, though of a preliminary nature, provides evidence that the ionisation reaches a minimum value for electrons of energy  $1.5 \times 10^6$  e.v., and beyond this minimum, ionisation increases roughly as predicted by the theory. Their observations, however, were restricted to relatively narrow range of energy and only to electronic component of Cosmic rays, and as such, left room for further investigations on the same line for electrons of higher energy and also for meson and proton components of Cosmic rays.

The total ionisation of Cosmic ray particles has been measured by the author in the energy range  $2 \times 10^6$  e.v. to  $3 \times 10^9$  e.v. This paper is concerned, firstly, with the experimental verification of the energy-ionisation relation for electrons up to ultra-relativistic region and, secondly, with the preliminary investigation of energy ionisation relation for mesons and protons.

## EXPERIMENTAL METHOD

The present investigation was carried out by the cloud chamber method at the suggestion of Prof. Blackett in his laboratory during the years (1938-40). The apparatus was essentially the same as described by Blackett (1936), though many mechanical improvements were made. The improvement consists in making the chamber completely automatic to the extent that no attention was needed even during the long periods of operation. Three different fields were used in the investigation; 350 gauss for particles in energy range  $1 \times 10^6$  e.v. to  $1 \times 10^7$  e.v., 2500 gauss for the range  $1 \times 10^7$  e.v. to  $3 \times 10^8$  e.v. and 8500 gauss for the range  $3 \times 10^8$  e.v. to  $3 \times 10^9$  e.v.

The chamber was enclosed in a copper box which helped to keep the temperature of the chamber as uniform as possible and thus reduced the track distortion. The gas mixture in the chamber was 90% argon and 10% oxygen and the condensant was 70% ethyl alcohol and 30% water.

In order to obtain sufficient diffusion of the track to enable the counting of the individual ions, a delay of the order of one-tenth of a second was introduced between the arrival of the particle and the expansion. This delay was controlled by the discharge of a condenser through a resistance.

The experimental arrangement was as follows. One camera placed at right angles to the chamber photographed the tracks for energy measurements, another camera placed at the side of the chamber took photographs of the same tracks by reflection on an aluminised glass mirror placed at  $22\frac{1}{2}^\circ$  to the axis of the chamber. By this method both the positive and the negative ions along the tracks, separated by an electric field between the front and the back of the chamber could be photographed and separately counted. Any loss of ions of one sign could thus be checked by comparing the number of ions per cm. in each branch of the track. Since the drops were photographed in the side camera by light scattered at  $45^\circ$  to the direction of incidence, the intensity of the scattered light was at least ten times the light scattered in the normal direction (Webb, 1935). Because of this gain in intensity, an aperture  $f/6.5$  could be used for the side camera, and the entire illuminated depth of the chamber could thus be brought into sharp focus.

Tracks of small curvatures were measured by the optical null method (Blackett, 1937) and those of larger curvatures were measured by the superposition of curves of known radii. For broad tracks, this method is superior to the usual practice of measuring co-ordinates, since it makes use of the whole photographic track as opposed to a finite number of points on it. The chamber distortion was determined by taking at regular intervals, throughout the experiment, photographs of tracks without the magnetic field. Measurements of twelve such tracks gave the mean curvature  $c = 0.4m^{-1}$ . The mean curvature without field obtained by Blackett (1937) working with the same chamber with practically no delay was of the order  $0.05m^{-1}$ . A decrease in delay would no doubt reduce the distortion and increase the maximum detectable energy but it would also reduce the diffusion of the track which is essential for counting droplets along the tracks. A compromise was thus necessary, and a delay of the order of one-tenth of a second was found to be most suitable.

## RESULTS AND DISCUSSIONS.

In 5,000 photographs taken altogether, there were 112 electron tracks in which both energy and ionisation were measurable. About a 100 meson tracks were also selected out of them for similar measurements. In all, only eight proton tracks were photographed, of which six could be used for ionisation measurements. The classification of the tracks were made in the following way —

1. In general, all shower particles were assumed to be electrons with the exception of a few particles of energy  $10^8$  e.v., which were considered to be mesons responsible for the production of 'knock on' showers (Bhabha, 1938). It is clear that only one particle in a shower can be a meson. Three such particles were neglected in 40 measured showers on the ground that their ionisation and energy were consistent with their being mesons.

2 Single particles with energies less than  $40 \times 10^6$  e v not exhibiting abnormally large ionisation were taken as electrons

3 Single particles in the energy region  $2 \times 10^8$  e v to  $7 \times 10^8$  e v showing heavy ionisation were taken to be protons

4 All other single particles were taken as mesons

Finally all the tracks were divided into eight energy groups and the mean ionisation in each group was estimated by taking the average of the mean ionisation per cm of each individual track in the group. The numerical results of all observations are summarised in the following table —

Energy range in e volts	Mean ionisation per cm of the track at N T P					
	Electron		Meson		Proton	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
$1 \times 10^6 - 5 \times 10^6$	36	$38.0 \pm 0.7$				
$5 \times 10^6 - 1 \times 10^7$	40.5	$42.5 \pm 0.6$				
$1 \times 10^7 - 5 \times 10^7$	46	$48.5 \pm 0.6$				
$5 \times 10^7 - 1 \times 10^8$	53	$54.5 \pm 0.8$				
$1 \times 10^8 - 5 \times 10^8$	56	$56.5 \pm 1.5$	36	$41.5 \pm 6$		
$5 \times 10^8 - 1 \times 10^9$	65	$63.0 \pm 2.1$	39	$41.0 \pm 6$	82	
$1 \times 10^9 - 3 \times 10^9$			41	$42.5 \pm 8$		
Energy above $3 \times 10^9$			40	$47.0 \pm 5$		
						$77 \pm 1.8$

In order to compare the experimental results with the theory let us work out the ionisation for electrons, protons and mesons separately

It is easily seen that

$$\begin{aligned}
 W_m &= mc^2 \gamma (\gamma - 1) && \text{for electrons,} \\
 &= \frac{2mc^2 (\gamma^2 - 1)}{1 + \frac{2m\gamma}{M_p}} && \text{for protons, and} \\
 &= \frac{(\gamma^2 - 1) 2mc^2}{1 + \frac{2m\gamma}{M_m} + \frac{m^2}{M_m^2}} && \text{for mesons,}
 \end{aligned}$$

where  $M_p$  = mass of the proton, and  $M_m$  = mass of the meson

There is, however, some doubt as to whether Bhabha's theory of collision can apply to that between electron and electron, for, as we see from the above expression, if an electron with energy  $\gamma mc^2$  directly encounters a stationary electron, it gives the energy  $(\gamma - 1)mc^2$  to the latter and is itself reduced to rest. The total energy of the struck electron is now  $\gamma mc^2$ , i.e. the rôles of the two electrons are reversed now. But one can easily see that such an event cannot take place, because most of the energy of the electron will be wasted in radiation. It is expected that the value of  $W_m$  when the ionising particle is an electron is much less than  $(\gamma - 1)mc^2$ , but no lead on this point appears so far to have been given by theoretical workers on the subject.

It can now easily be shown that for the electron, the minimum ionisation is obtained for a value of  $\gamma$  which satisfied the equation

$$\frac{1}{(\gamma^2 - 1)^{\frac{1}{2}}} \left( 4 - \frac{1}{\gamma^2 (1 + \gamma^2)^{\frac{1}{2}}} \right) - \frac{2}{(\gamma^2 - 1)^{\frac{1}{2}}} \left\{ \log \left( \frac{mc^2}{IZ} \right)^2 + 4 \log (\gamma^2 - 1)^{\frac{1}{2}} - 1 - \log (\gamma + 1) - \frac{(\gamma^2 - 1)}{\gamma^2} \right\} = 0.$$

This gives us  $\gamma = 3.5$ , for  $W_m = (\gamma - 1)mc^2$  at energy of  $1.75 \times 10^6$  e.v. and the value of  $-\frac{dE}{dx}$  comes out to be 61 ions per cm. The number of ions per cm. observed in the energy region  $1 \times 10^6$  e.v. is, however, only  $38 \pm 7$ . This discrepancy between the theoretical and experimental values is too large to be accounted for by the inaccuracy of the observation. This confirms our contention that  $W_m$  is not given by  $(\gamma - 1)mc^2$  at least in the case of the electron.

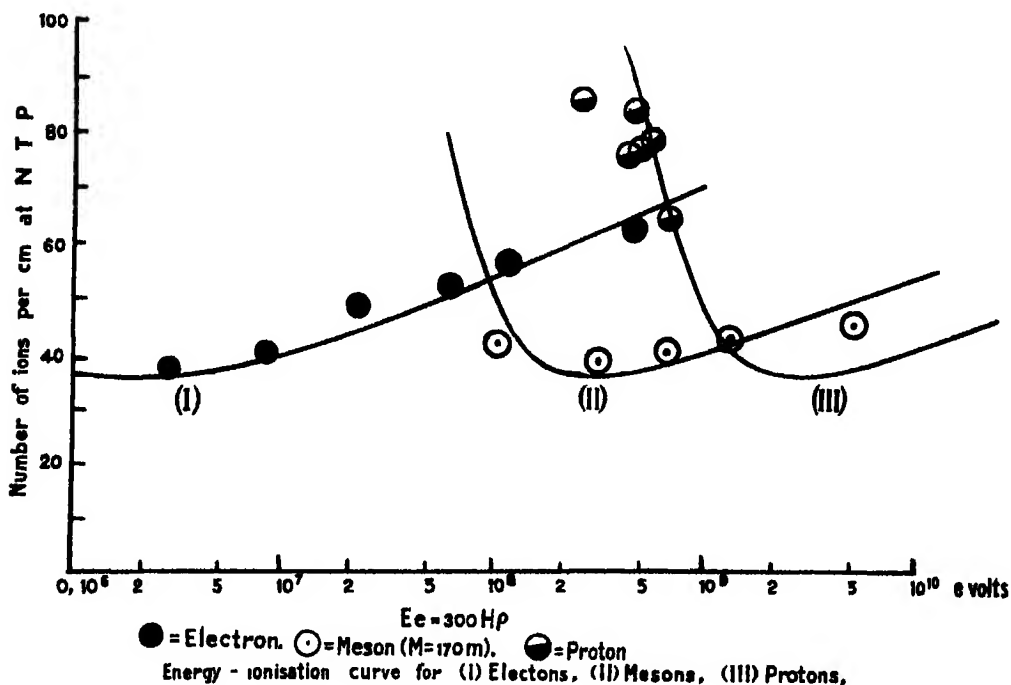


FIG 1.

For mesons (mass =  $170m$ ) and protons,  $W_m \approx 2mc^2(\gamma - 1)$  and  $-\frac{dE}{dx}$  attains a minimum for a value of  $\gamma$  satisfying the relation

$$1 - \log 2 - \log \frac{mc^2}{IZ} - 4 \log \sqrt{\gamma^2 - 1} + 2(\gamma^2 - 1) = 0$$

This equation is satisfied for  $\gamma = 3.2$ , the corresponding energy being  $2.72 \times 10^8$  e.v. for mesons and  $2.944 \times 10^9$  e.v. for protons. For mesons the theoretical value of  $-\frac{dE}{dx}$  corresponding to this energy comes out to be 68 ions per cm. (taking 33.5 e.v. = the energy used up per ion) against the experimental value of  $41.5 \pm 6$  ions per cm. observed in the energy region between  $1 \times 10^8$  e.v. to  $5 \times 10^8$  e.v. We observe that in the case of electrons as well of mesons the agreement between the theoretical and experimental values of specific ionisation is far from being satisfactory. It is to be noted, however, that the region of energy determined experimentally, in which the minimum ionisation takes place, is rather flat (from  $\gamma = 1.17$  to  $\gamma = 1.17$ ) and coincides with the region of minimum ionisation determined by theoretical considerations.

For protons, only one point on the curve could be obtained and detailed comparison could not be made with the theory.

The expression  $W_m = (\gamma - 1)mc^2$  for electrons is, therefore, not supported by the present experimental results. Either there is something wrong with the counting of particles, or the formula for ionisation requires modification.

As regards the second point, it is almost certain that we are not justified in putting the mean energy of ionisation  $I(Z)$  where  $I = 13.54$  e.v.,  $Z =$  atomic number. For nitrogen, it comes out to be about 95 volts. But the mean energy of ionisation is known to be 35 volts.

Putting  $I(Z) = 35$  volts (Conduction of Electricity by Gases, by Thomson and Thomson, p. 103) in the expression for  $-\frac{dE}{dx}$  in the case of mesons, and leaving  $W_m$  unaltered for the present, we find that for mesons the minimum value of  $-\frac{dE}{dx}$  is obtained for  $\gamma = 8.8$ , i.e. when  $E = 7.5 \times 10^8$ . This is inside the flat region, but the value of  $-\frac{dE}{dx}$  at this point is 86 ions. The agreement is therefore worse than before.

Another adjustment is possible if  $W_m$  is varied. It can easily be shown that for  $I(Z) = 13.5Z$  volts, we obtain the minimum observed value of 38 ions for electrons, if  $W_m = 1187$  e.v., and minimum observed value of 41 ions for mesons, if  $W_m = 1127$  e.v.

There is some evidence that the value of  $W_m$  is of the above order, for, if we look at the tracks carefully, we find that the number of particles along the track is not uniform throughout but some clusters are found at intervals. We may take these clusters as marking the points where the ionising particle imparts fairly large energy to the struck electrons, which produce large number of secondary electrons and thus lead to the formation of clusters. The maximum number of ions countable in a cluster, in the present experiment was 40, hence  $40 \times 33.5$  e.v. = 1340 e.v. is the maximum energy transferred to a secondary electron. If we identify this with  $W_m$ , the discrepancy between the theoretical and experimental values vanishes.

The theoretical energy ionisation curve for electrons has been drawn in Fig. 1, curve I, with this value of  $W_m$ . The shaded circles are the mean ionisation per cm. for electrons in different energy groups. The agreement of the experimental points with the theory is quite satisfactory up to  $5 \times 10^8$  e.v. It is also seen that the specific ionisation of electrons of energy  $5 \times 10^8$  e.v. is about 52% higher than that of a meson of the same energy, as is demanded by the theory. This agreement also gives a further evidence of the validity of the relativity theory up to ultra-relativistic region, as modified above.

The theoretical curve for mesons ( $170m$ ) has been shown in Fig. 1, curve II. The open circles represent the mean observed ionisation at different energy intervals. The statistical error in each case is less than  $\pm 1$ . The maximum detectable energy was  $3 \times 10^9$  e.v. All the measured tracks above this energy were included in the last group, the mean energy being calculated on the assumption of  $\frac{1}{E^2}$  spectrum.

Although the experimental value of specific ionisation of mesons at the first and last point is slightly lower than the theoretical value, there is a definite indication of the increase in ionisation with energy beyond  $2 \times 10^8$  e.v. The chance that the observed increase is due to fluctuation is negligible. Since the higher energy tracks used for the determination of the last point on the meson curve may partly be due to protons, and since in this region protons ionise less than mesons, the actual ionisation for the mesons alone should be larger. A mixture of 10% proton and 90% meson would give rise to the observed deviation from the theoretical value.

In three thousand tracks photographed altogether, 8 heavy tracks of energy between  $2 \times 10^8$  e.v. to  $6 \times 10^8$  e.v. were observed all of which can be attributed to protons. The observed specific ionisation for protons has been plotted in Fig. 1, curve III, in half shaded circles. The experimental points do not show any large departure from the theoretical curve for protons. Large deviations from theoretical curve, however, are expected since the curve in this region is steep and the density of ions per cm. along the tracks reaches nearly the

maximum number which could be counted. All the protons observed were of positive character, no deuteron or  $\alpha$ -particle was observed.

I wish to express my sincere thanks to Prof P M S Blackett, F.R.S., for his invaluable help and encouragement. I also wish to express my gratitude to Prof E J Williams, F.R.S., for helpful discussions. My thanks are due to Mr A H Chapman for his substantial help in taking the photographs. I am also indebted to the Department of Scientific and Industrial Research (England) for a grant to enable this work to be completed.

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Photograph of a partially diffused shower taken with a magnetic field 8500 Gauss. The positive and negative ions along the tracks are just separated to be individually recognised. From energy and ionisation measurements one concludes that the least curved track in the group is a meson. The energy of the slowest particle in the shower is  $1 \times 10^7$  e.v.

(The author regrets that the photographs of well diffused tracks suitable for accurate measurements which were actually used in this investigation are not available just at present and so could not be reproduced.)



# EXCITATION PROCESSES OF THE NIGHT SKY SPECTRUM

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(Communicated by Prof S K Mitra, F N I)

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## ABSTRACT

The paper discusses the hypothesis recently proposed by Mitra (1943) for the excitation of the night sky spectrum. Region-F of the ionosphere which contains at night  $N_2^+$  and  $O^-$  ions is identified in the hypothesis as the luminescent layer. The  $N_2^+$  and  $O^-$  ions are assumed to react in the following manner



The following noteworthy features of Mitra's hypothesis are discussed. Exact resonance is obtained when the oxygen atom and the nitrogen molecule are excited precisely to those levels from which the observed lines and bands are emitted. O atom is excited to  $^1S$  state, this leads to the emission of the green and red lines.  $N_2$  molecule is excited to  $B^3\Pi$  level, this leads to the emission of the first positive and Vegard-Kaplan bands. If account is taken of the kinetic energy of the colliding particles then the levels  $v'=10, 11, 12$ , of  $B^3\Pi$  level are also excited. Emissions due to transitions from those levels are just those that are found enhanced in the night sky spectrum.

Unlike the hypotheses proposed so far the present hypothesis explains the excitation of the atomic lines and the  $N_2$ -bands by a single reaction.

Another possible reaction between  $N_2^+$  and  $O^-$ ,



which, for lack of exact resonance, is necessarily less probable explains the occurrence of the weak  $\beta$  and  $\gamma$  bands of NO and of the atomic nitrogen line  $\lambda 3467$ .

Attention is drawn to the fact that according to the proposed hypothesis the electrons disappear by a recombination process which is controlled by the density of negative ions formed by attachment of electrons to oxygen atoms. A satisfactory consequence of this is that the intensity of emission, in course of the dark hours of night, remains fairly constant, though, during the same period, the electron density in the region of maximum density may fall comparatively rapidly.

The intensity of the green line has been calculated on the basis of the above hypothesis. The result is found to agree with Lord Rayleigh's measurements (Rayleigh, 1930). The slightly lower intensity of the red lines is found to be a simple consequence of the hypothesis.

The unsatisfactory nature of some of the hypotheses proposed so far is also discussed.

A satisfactory explanation is given of the enhancement of the red lines at twilight as recently observed by Elvey and Farnsworth (1942).

## 1 INTRODUCTION

The spectrum of the night sky luminescence consists, as well known, mainly of lines of atomic oxygen and of band systems of molecular nitrogen (see Fig.). The atomic oxygen lines are the so-called auroral green,  $^1S \rightarrow ^1D$  ( $\lambda 5577$ ), and red lines,  $^1D \rightarrow ^3P_2, 1$  ( $\lambda 6300, \lambda 6363$ ), both due to forbidden transition. The green line is the most prominent radiation of the night sky light. The  $N_2$ -bands are represented by the first positive bands,  $B^3\Pi \rightarrow A^3\Sigma$ , which are comparatively faint and the Vegard-Kaplan bands,  $A^3\Sigma \rightarrow X^1\Sigma$ , which are stronger. Besides these there are probably also present band systems of NO and a forbidden line of atomic nitrogen,  $^2P \rightarrow ^4S$  ( $\lambda 3467$ ). The identification of these is still somewhat doubtful.

The intensity of the night sky emission is not constant. It consists of a quasi-steady as well as of an irregularly fluctuating part. The variations of the latter show strong correlation with magnetic activity and, as such, its excitation is believed to be due to the same

cause as that of the aurora (Barber, 1941). The ultimate source of energy of the quasi-steady part is the ultra-violet radiation of the sun. The radiation ionises and dissociates the upper atmospheric constituents during daytime. The products of these processes react with each other at night and in course release the stored energy as faint luminescence. The precise reaction or reactions between the ionised and dissociated bodies which may excite the night sky spectra are, however, by no means easy to predict. Many hypothetical processes have been proposed from time to time, but they have all been unsatisfactory for one reason or other (Chapman, 1937, Martyn and Pulley, 1936, Ta-You Wu, 1943). It is the purpose of this paper to discuss in detail a process of excitation which has recently been suggested by Mitra (1943) and which, it will be shown, is the most satisfactory hypothesis offered till now.

### *Region-F of the ionosphere identified as the luminescent layer*

As already mentioned, the night sky emission—at least the quasi-steady part of it—represents the energy spent by the solar ultra-violet radiation in daytime in ionising and/or dissociating the upper atmospheric constituents. In the various hypotheses proposed till now, it is the energy of dissociation which has been assumed to provide a mechanism for the night sky luminescence. Mitra, however, makes a departure and assumes that the luminescence is related rather to ionisation than to dissociation of the upper atmospheric constituents. He, therefore, identifies Region-F of the ionosphere extending from 200 to 400 km, as the active layer, since, measurements show that the height of the luminescent layer is much above 100 km (Cabannes and Dufay, 1934) and may be nearer to 500 km (Elvey and Farnsworth, 1942). (It is to be remembered that the methods of height measurement of the luminescent layer are unfortunately such as to yield only very rough result, merely indicating the region of the upper atmosphere in which it may be situated.)

The constituents of the atmosphere above 100 km are atomic oxygen and molecular nitrogen. The prevalence of atomic oxygen is due to the photo-dissociation of  $O_2$  during daytime by absorption of ultra-violet radiation  $\lambda < 1750$ . Theoretical calculations show that the dissociation commences from the height of 80 km, and above 130 km it is practically complete (Majumdar, 1938, Wulf and Deming, 1938).

During daytime Region-F is split up into two ionised regions  $F_1$  and  $F_2$ .  $F_2$ , which is at a higher level, is due to ionisation of atomic oxygen and  $F_1$  at a lower level is due to ionisation of molecular nitrogen. Presence of  $N_2^+$  in the upper atmosphere is proved on unimpeachable grounds by the fact that spectrograms of the eastern and western skies during twilight show negative bands of nitrogen (Slipher, 1933, Elvey, 1942). These bands are due to the transition  $^2\Sigma_u \rightarrow ^2\Sigma_g$  of  $N_2^+$ . Solar radiation  $\lambda < 661$  excites and ionises  $N_2$  molecules to the  $^2\Sigma_u$  state (Bhar, 1938). These, on emission of the negative bands, drop and remain in the  $^2\Sigma_g$  state. The  $F_1$  and  $F_2$  regions coalesce at night to produce a single region F. This region, therefore, contains besides  $N_2$  and O, the positive ions  $N_2^+$ ,  $O^+$  and electrons. Further, the region contains negative oxygen ions ( $O^-$ ). It is now recognised that in Region-F at night attachment of electrons to oxygen atoms as also their detachment from same produce an equilibrium condition, in which the negative ion ( $O^-$ ) density is about 10 times that of the electron density (Bates and others, 1939). These charged and uncharged particles react with each other at night, in course of which the faint light, observed as the light of the night sky, is emitted.

The nightly densities of the different particles in the region of maximum ionisation of Region-F may be taken as follows:—

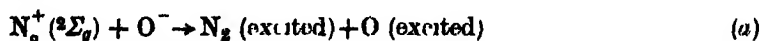
Electron density	..	$5.0 \times 10^8$ per c.c.
Density of $O^-$	..	$5.0 \times 10^8$ per c.c.
Density of positive ions ( $N_2^+$ and $O^+$ )	..	$5.5 \times 10^8$ per c.c.
( $N_2^+$ ion density is one order less than that of $O^+$ )		
Density of atomic oxygen	..	$1.4 \times 10^{11}$ per c.c.

It is to be noted that the average nightly densities of the ionised particles vary not only with the season of the year, but also markedly with the eleven-year solar cycle. The values given may be taken as representative values for a period midway between the epochs of maximum and minimum solar activity.

## 2 EXCITATION OF THE NIGHT SKY SPECTRUM—MITRA'S HYPOTHESIS

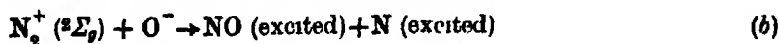
Many possible reactions, as are likely to excite the night sky spectrum, may be imagined to occur between the different kinds of particles listed above. Not all of them, however, could be the reactions actually occurring in the luminescent layer. The most probable reaction will be the one, which is not only plausible but which, at the same time, gives reasonable explanation of most of the observed characteristics of the night sky luminescence. In particular, the reaction must explain the observed intensity of the emission. Further, the height of the region of the reaction must conform with the observed height of the luminescent region, i.e. it must lie much above 100 km and nearer to 500 km.

The reaction which offers the best explanation of the features is the one recently proposed by Mitra (1943). It involves a reaction between the positive ions of nitrogen molecule and negative ions of atomic oxygen, both of which are present in the Region F' (combined  $F_1$ ,  $F_2$ ) at night



The process is one of so-called electron transfer and has a high probability when the resonance condition is satisfied, i.e. when the energy released by the neutralisation of the charged particles is taken up entirely as potential energy of excitation of the reaction products. A very satisfactory feature of the proposed reaction is that the condition of resonance is satisfied when the levels of excitation of the O atom and the  $\text{N}_2$  molecule are just those that are required for the emission of observed lines and bands of O and  $\text{N}_2$ . Since the ionisation potential of  $\text{N}_2$  for ionisation to  $\text{N}_2^+ (^2\Sigma_g)$  state is 15.58 e-volts, and the electron affinity of atomic oxygen is 2.2 e-volts (Lozier, 1934), the energy released on neutralisation is  $15.58 - 2.2 = 13.38$  e-volts. This energy is taken up almost entirely by  $\text{N}_2$  and O, if, on neutralisation the former drops to the vibrational level  $v'=9$  of  $B^3\Pi$  state (9.1 e-volts) and the latter is excited to the  $^1S$  state (4.2 e-volts). The  $\text{N}_2$  ( $B^3\Pi$ ) molecule drops successively to the  $A^3\Sigma$  state and thence to the  $X^1\Sigma$  state and in course emits the first positive and the Vegard-Kaplan bands respectively (see Fig.). If account is taken of the thermal energy of the colliding particles (average value 0.26 e-volt corresponding to temperature 1000°K) then to accommodate it the neutralised  $\text{N}_2$  molecule will drop to the vibrational levels  $v'=10, 11, 12$ . The emissions corresponding to transitions from these levels are just those that are found enhanced in the first positive band system of the night sky spectrum.

Another possible reaction between  $\text{N}_2^+$  and  $\text{O}^-$  is as follows.—

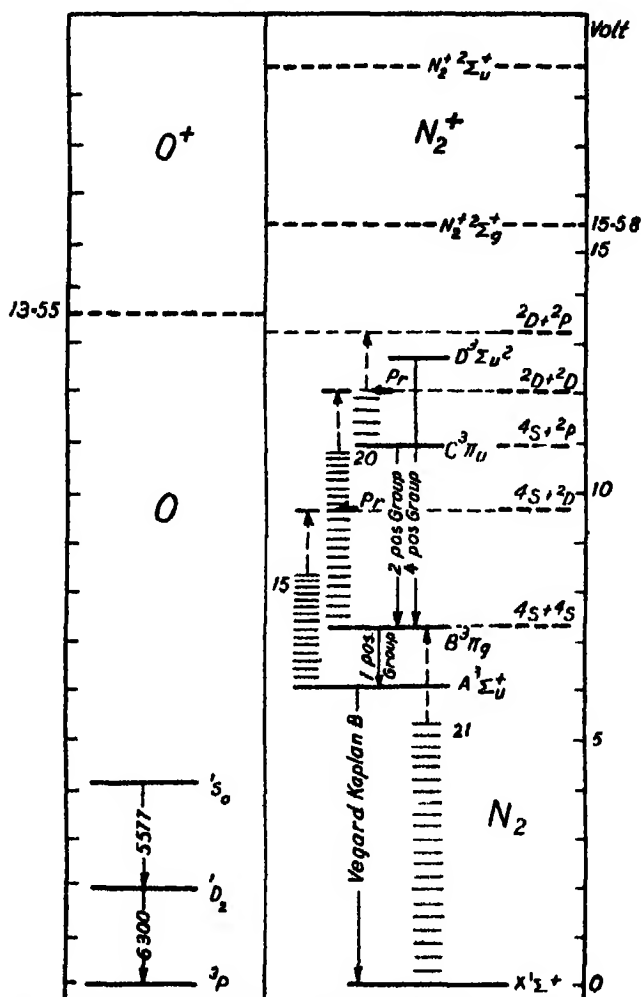


The energies of the levels ( $B^3\Pi$  for NO and  $^2P$  for N), which would emit the observed  $\beta$  and  $\gamma$  bands of NO and a line  $\lambda 3487$  of atomic nitrogen, do not correspond to exact resonance. As such, the probability of the reaction is much smaller than the probability of reaction (a). However, the reported presence of these weak bands and line may be traceable to this reaction.

At the vibrational level  $v'=13$  of  $B^3\Pi$  state of  $\text{N}_2$  the molecule is predissociated. For particles with energy greater than the average kinetic energy, reaction (a) will produce two nitrogen atoms, one in the ground state  $^4S$  and the other in the excited state  $^2D$ . This reaction, if it occurs, would lead to the emission of  $^2D \rightarrow ^4S$  ( $\lambda 5200$ ). No such line has, however, been reported till now.

A noteworthy feature of the proposed hypothesis is that one single reaction (a) excites both atomic oxygen lines and  $\text{N}_2$ -bands. In the various other hypotheses suggested till

now two sets of reactions are generally proposed, one for excitation of the oxygen lines and the other for excitation of the  $N_2$ -bands



Energy level diagrams of O and  $N_2$  illustrating the excitation processes of night sky spectrum

The proposed reaction being a Region-F reaction, some correlation may be expected between variations of Region-F electron density and the variations of intensity of night sky emission. In attempting to study such correlation, two facts, however, have to be borne in mind. Firstly, the electron density as obtained from ionospheric measurements is the density in the region of maximum ionisation. It does not tell us anything about the total number of electrons present in a column of say of unit cross-section of the region. The intensity of the night sky luminescence depends, however, precisely upon this latter quantity. The electron density, for instance, may increase due to contraction by cooling of the ionised region as a whole, but the total number of electrons in a column of unit cross-section will remain more or less constant. For such case, though the radio measurements will record an increase in electron density, there will be no corresponding increase in the intensity of emission. Again, for recombination according to the proposed reaction, the variation of electron density with time will be given by the formula (Bates and others, 1939)

$$n(t) = \frac{n(0)}{1 + 10\alpha_i n(0)t},$$

where  $n(0)$  is the initial value of electron density and  $\alpha_i$  the coefficient of recombination,  $2 \times 10^{-11}$  cm<sup>3</sup>/sec (see § 3). The value of the ratio  $n(t)/n(0)$ , therefore, depends on the initial density  $n(0)$ , being smaller the greater its value. In a vertical column of the ionised region with a parabolic gradient of ion density (see § 3) the decay in the total number of electrons will therefore be far less than the decay in the density in the region of maximum ionisation. For instance, if the maximum concentration be  $5 \times 10^5$  per c.c., its value will be reduced to about one-fourth for an eight-hour decay. On the other hand, in the region in which the concentration is  $10^5$  per c.c., the value in the same length of time will be reduced only to  $1/16$ . It, therefore, follows that the intensity of night sky emission will be far more constant throughout the dark hours than the electron concentration in the region of maximum ionisation. This is exactly what is found from observation (Elvey, 1943). However, the average variations of intensity for cycles of long period, e.g. seasonal variations, variations with eleven-year solar cycle, do show some correlation between the two phenomena as they ought to.

It is to be noted that according to reaction (a), it is the electron attached to the negative ion  $O^-$  which neutralises the positive ion  $N_2^+$ . The process by which the electrons in the ionised regions disappear at night is, therefore, a recombination process which is controlled by density of negative ions. This is very satisfactory because it has been found that the measured rate of electron decay can be explained by such a process only (Bates and others, 1939).

### 3 CALCULATION OF THE INTENSITIES OF THE GREEN AND THE RED OXYGEN LINES

We will now discuss if the proposed reaction (a) can explain the observed intensity of the green auroral line.

The rate at which oxygen atoms arrive in the excited  $^1S$  state is given by

$$\alpha_i n^+ n^-$$

where  $\alpha_i$  = coefficient of recombination by electron transfer from negative to positive ions. Assuming that the efficiency of the reaction is unity, i.e. every collision is successful in producing the reaction, the value of  $\alpha_i$  becomes  $2 \times 10^{-11}$  cm<sup>3</sup>/sec.

$n^+$  = concentration of  $N_2^+$  ion in Region-F at night

$n^-$  = "  $O^-$  "

The rate at which the reaction,  $^1S \rightarrow ^1D$  ( $\lambda$  5577), proceeds is a fraction of the above given by

$$\alpha_i n^+ n^- \frac{A_1}{A_1 + A_2}$$

where  $A_1$  = probability of  $^1S \rightarrow ^1D$  transition,  $2.0 \text{ sec}^{-1}$

$A_2$  = "  $^1S \rightarrow ^3P_1$  "  $0.18 \text{ sec}^{-1}$

(Probabilities of  $^1S \rightarrow ^3P_{2,0}$  transitions are negligible)

Since the concentrations of  $N_2^+$  and  $O^-$  are taken respectively equal to and ten times the electron density  $n$ , the above expression reduces to

$$10\alpha_i n^2 \frac{A_1}{A_1 + A_2}$$

In order to determine the total number of transitions per second in a column of gas of 1 sq cm cross-section, we assume that the electron density with height follows a parabolic law (Appleton, 1939),

$$n_e(h) = n_e(0) \left( 1 - \frac{h^2}{4H^2} \right),$$

where  $H$  is the scale height, which, according to radio measurements may be taken as 50 km. The total number of transitions taking place in a column of 1 sq cm cross-section per second is, therefore, given by

$$\begin{aligned} & 10\alpha_i \frac{A_1}{A_1 + A_2} \int_{h=-2H}^{h=2H} n_e^2(h) dh \\ &= 10\alpha_i \frac{A_1}{A_1 + A_2} n_e^2(0) \int_{h=-2H}^{h=2H} \left( 1 - \frac{h^2}{4H^2} \right)^2 dh \\ &= \frac{64}{3} \alpha_i \frac{A_1}{A_1 + A_2} n_e^2(0) H \\ &= 4.9 \times 10^8 \text{ transitions per second} \end{aligned}$$

This is of the same order as  $1.8 \times 10^8$  per sec obtained by Rayleigh (1930). It should be mentioned that the calculation is to be regarded as giving only a rough estimate of the order of the emitted intensity. This is because the distribution of electron density has been assumed as following a parabolic law throughout the entire thickness of the layer. This is not correct. It is only near the region of maximum density that the parabolic law holds with 5% accuracy within a thickness  $2H$ . Above height  $H$ , the electron density falls much less rapidly. The calculated intensity is therefore too low on this account. Again, it has been assumed that the electrified particles of the two regions are thoroughly mixed. We do not know to what extent such thorough mixing takes place in course of the night. Finally, on account of the high probability of reaction (a) its value has been taken as unity, the actual value may be somewhat different and not exactly equal to unity.

For the red radiation, it is to be noted that of the atoms that have been excited to  $^1S$  state, a fraction  $\frac{A_1}{A_1 + A_2}$  drops first to  $^1D$  state in course of emission of  $\lambda 5577$  and thence to the ground state  $^3P_{2,1}$  emitting the red lines  $\lambda 6300$  and  $\lambda 6363$  (The transition  $^1D \rightarrow ^3P_0$ , on account of its low probability, is neglected). The other fraction  $\frac{A_2}{A_1 + A_2}$  of  $^1S$  atoms, which is 11 times less than the fraction  $\frac{A_1}{A_1 + A_2}$  drops to the  $^3P_1$  state and emits the trans-auroral line  $\lambda 2972$ . Its absence in the night sky spectrum is due to the fact that it lies beyond the limit of transparency of atmosphere. The rate of the reaction,  $^1S \rightarrow ^1D$ , is thus practically equal to the rate of the reaction,  $^1D \rightarrow ^3P_{2,1}$ . The ratio of the intensity of the green radiation to the integrated intensity of red radiations should, therefore, merely be proportional to the energies of these radiations. This ratio is 1.13 and the red radiation is, therefore, slightly fainter than the green radiation. This is in accordance with observations (Elvey and Farnsworth, 1942).

#### 4 OTHER SUGGESTED PROCESSES

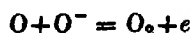
As mentioned in the introduction, the energy of night sky emission is to be traced ultimately to that of solar ultra-violet radiation spent during daytime in dissociating and/or ionising the atmospheric constituents. In the hypothesis of Mitra, it is the energy spent in ionisation that is re-emitted at night. Since, however, a large amount of energy is

also spent in process of dissociation  $O_2 \rightarrow O + O$ , it is tempting to suggest that the night sky emission represents this latter energy. The earliest suggestion in this connection was made by Chapman (1937). He imagined a three-body recombination process as follows —



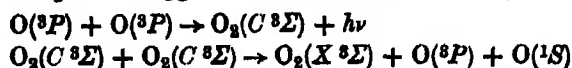
in which the third body  $M$  takes up the energy released on the recombination of the two  $O$  atoms to form  $O_2$ . According to Chapman, the third particle may be another oxygen atom or a nitrogen molecule. The excited oxygen atom and nitrogen molecule may thus give rise to the atomic oxygen lines and the  $N_2$ -band systems. Three-body collision process, however, is essentially a high pressure phenomenon. Its probability is extremely small in the low pressure of Region- $F$  ( $3 \times 10^{-5}$  mm of Hg), and it is, therefore, unlikely that this process makes any contribution to the intensity of night sky emission.

Reference may be made in this connection to an ingenious suggestion made by Martyn and Pulley (1936) which obviates the necessity of a simultaneous collision of three bodies which is such a rare event in the tenuous upper atmosphere. Thus in the following reaction,



the electron attached to the negative ion acts as the third body carrying away the released energy as kinetic energy. Martyn and Pulley supposed that the ejected electron has energy of 4 e-volts, and that when it collides with an oxygen atom it excites the atom to  $^1S$  state. Closer inspection shows, however, that the ejected electron can have energy of only 2.89 e-volts and not 4 e-volts. This is because the dissociation energy of molecular oxygen giving rise to two normal oxygen atoms (instead of one in the  $^3P$  and the other in the  $^1D$  state) is 5.09 e-volts. The energy imparted to the ejected electron is, therefore, 5.09 e-volts less the detachment energy of electron from negative oxygen ion (2.2 e-volts). This reaction can, therefore, at best explain the emission of red auroral lines.

Very recently another attempt has been made at explaining the night sky emission with the help of dissociation energy rather than ionisation energy by Ta-You Wu (1943). For this purpose the author supposes that not only  $O_2$  but also  $N_2$  is dissociated in the upper atmosphere. The process suggested for the excitation of oxygen lines is as follows —



In the first step recombination of  $O$  atoms in the normal state is accompanied by radiation and the resulting  $O_2$  molecule is excited to the metastable  $C^3\Sigma$  state. Two  $O_2(C^3\Sigma)$  molecules then react with each other and produce one normal oxygen molecule and two  $O$  atoms. By making assumptions regarding the probabilities of these two processes and assuming a high metastability of the  $O_2(C^3\Sigma)$  molecule, and also taking the density of the  $O$  atoms to be  $10^{10}$  per c.c., the author calculates the intensity of the green line emission and obtains agreement with the observed value. Based on the many assumptions, as it is, the agreement cannot, however, be regarded as a satisfactory evidence in support of the hypothesis. It is at best one of the many possible processes which may cause the green line emission. How greatly the deductions depend upon the assumptions made is seen from the following. The author, as mentioned above, has assumed the density of atomic oxygen to be  $10^{10}$  per c.c. Theoretical calculations show, however, that the oxygen molecules begin to be dissociated from below the level of  $E$  layer and is practically wholly dissociated at a height of 130 km (Majumdar, 1938, Wulf and Deming, 1938). Its region of maximum concentration lies in the neighbourhood of 84 km ( $10^{14}$  atoms per c.c.). At 130 km. the concentration is  $10^{12}$  per c.c. If these data are adopted for calculating the intensity of the green line according to the author's hypothesis, then the result obtained is many orders higher than the observed intensity. There are also other serious difficulties. As mentioned just now the region of maximum density of oxygen lies in the neighbourhood of 84 km. According to this hypothesis, therefore, the region of emission of the atomic oxygen lines should also lie in this region. As already mentioned, measurements show that the luminescent layer lies much above 100 km. Again, according to the

hypothesis, presence of photo-dissociated nitrogen atoms is essential for emission of  $N_2$ -bands. Photo-dissociation of  $N_2$  in the upper atmosphere by absorption of solar radiation is however very doubtful. No continuous absorption corresponding to photo-dissociation has been observed in case of molecular nitrogen as in the case of molecular oxygen. It is true that the presence of the line,  $^2P \rightarrow ^4S$  ( $\lambda$  3467) due to atomic nitrogen has been reported by some observers. This, however, can be simply explained by Mitra's hypothesis (Reaction (b)) without assuming the presence of photo-dissociated nitrogen atoms. Further, if  $N_2$  were photo-dissociated, its region of maximum density would be at a level different from that of atomic oxygen. The luminescent layer for the emission of  $N_2$ -bands would thus be also different from that of oxygen lines. This is not supported by observation.

## 5. ENHANCEMENT OF THE INTENSITY OF RED AURORAL LINES AT DAWN

Recently Elvey and Farnsworth (1942) in course of a series of interesting observations have noticed that as the sun begins to illuminate the upper atmosphere in the early hours of the morning the intensity of the red radiation shoots up to a high value, while that of the green radiation remains nearly the same. This shows that in addition to night time processes a new factor begins to operate at dawn whereby the concentration of  $O(^1D)$  atoms increases to a high value. It will be shown now that the rapid increase of red radiation is simply explained if transitions by absorption of solar rays are taken into account.

The solar rays stimulate normal oxygen atoms to excited states and those already in excited states to still higher or to lower levels. Since the population of atoms in the excited levels compared to that of neutral atoms is very small, the number of transitions of the former is negligibly small compared to the latter and need not be taken into consideration.

The number of normal oxygen atoms that are stimulated to  $^1D$  state per unit time per c.c. by absorption of solar radiation is

$$nB_2P_2 \rightarrow ^1D D\rho_{\nu_{6300}} \quad (1)$$

where  $n$  = concentration of normal oxygen atoms in Region-F at dawn

$D\rho_{\nu_{6300}}$  = density of solar radiation for the frequency corresponding to  $\lambda$  6300 in the topmost layer of atmospheric oxygen touched by the solar rays.  $D$  is the dilution factor due to distribution of quanta emitted by the sun over a surface  $4\pi d^2$  where  $d$  is the distance of the earth from the sun.  $D = R^2/4d^2 = 5.41 \times 10^{-6}$  where,  $R$  is the radius of the sun.

$B_2P_2 \rightarrow ^1D$  = probability for  $^3P_2 \rightarrow ^1D$  transition

If the radiation from the sun be assumed to be that due to a black body at temperature  $T_s = 6000^\circ K$ , then, since  $\exp(h\nu_{6300}/kT_s) \gg 1$ ,

$$\rho_{\nu_{6300}} = \frac{8\pi h\nu_{6300}^3}{c^3} \exp(-h\nu_{6300}/kT_s)$$

according to Planck's radiation formula

$$\text{Further, remembering that } \frac{B_2P_2 \rightarrow ^1D_2}{A_1D_2 \rightarrow ^3P_2} = \frac{c^3}{8\pi h\nu_{6300}^3}, \text{ equation (1) reduces to}$$

$$nA_3D \exp(-h\nu_{6300}/kT_s) \quad (2)$$

where  $A_3$  = probability of  $^1D \rightarrow ^3P_2$  transition,  $0.0075 \text{ sec}^{-1}$

The atoms arriving in  $^1D$  state will leave the state by (i) spontaneous transition to ground state  $^3P$  and (ii) by stimulated transition to some higher states or to the  $^3P$  state. Now, on account of the low value of  $D\rho_{\nu_{6300}}$  (of the order  $10^{-20} \text{ erg}$ ), the rate of the latter

transition is negligibly small compared to the former transition. We can therefore justifiably assume that in the equilibrium condition, the number of atoms raised to  $^1D$  state by stimulated transition per second as given in equation (2) is equal to the number dropping to  $^3P$  state by spontaneous transition.

Substituting the values of various terms in equation (2) we find that the increase in the rate of the reaction leading to the emission of red lines is 127.3. This is five times greater than the average night time rate, namely 24.5. The integrated intensity of the red lines at dawn therefore is greater than at night by this amount, and this is what has been observed by Elvey and Farnsworth (1942).

We now determine the intensity of the green radiation as affected by the solar rays. The rate at which normal oxygen atoms are stimulated to  $^1S$  state per cc by absorption of solar rays is

$$\frac{1}{5} n A_{1S \rightarrow 3P_2} D \exp(-h\nu/kT_s) \quad (3)$$

where  $\nu$  = frequency of radiation corresponding to  $^1S \rightarrow ^3P_2$  transition,

$A_{1S \rightarrow 3P_2}$  = probability of  $^1S \rightarrow ^3P_2$  transition. The factor  $(\frac{1}{5})$  comes from the consideration of the weights of the states.

The transition probability of  $A_{1S \rightarrow 3P_2}$  is known to be very small compared to the other transitions of the oxygen atom considered. The value of this probability may for the purpose of the present computation be taken to be one-tenth of that of  $A_4(^1D \rightarrow ^3P_1)$ , 0.0025 sec<sup>-1</sup>. Substituting the values of various terms in equation (3), we obtain the rate at which normal oxygen atoms are stimulated to  $^1S$  state per cc as 0.01 per second. This is very small compared to the night time rate, namely 24.5. We thus find that the intensity of the green line is hardly affected by the incidence of solar radiation at dawn.

The great difference in the effect of solar radiation on the enhancements of the green and red lines is thus due to the combination of two factors acting in the same sense. Firstly, the probability of stimulated transition of the O atoms from the ground state to the  $^1S$  state is very small compared to the stimulated transition to the  $^1D$  state and secondly, the density of radiation  $\lambda$  2972 corresponding to transition to  $^1S$  state is about 100 times smaller than the density of radiation  $\lambda$  6300 corresponding to transition to  $^1D$  state.

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## STUDIES IN THE FAMILY ALISMACEAE V

### THE EMBRYOLOGY OF *Machaerocarpus californicus* (TORR.) SMALL<sup>1</sup>

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#### INTRODUCTION

The embryology of the Alismaceae has recently received considerable attention at the hands of Prof. K. V. O. Dahlgren (Uppsala) and Dr. B. M. Johri (Agra). The literature on the family has been reviewed very fully by these authors (Dahlgren, 1928, 1934, Johri, 1935 a, b, and c, 1936a) and it is therefore unnecessary for us to cover the same ground again. The genera *Machaerocarpus* (California), *Rautanenia* (S. W. Africa), *Burnatia* (Trop. Africa and Madagascar), *Wiesneria* (India, Africa and Madagascar), *Caldesia* (N. Australia), and *Ranalisma* (Malaya) have not so far been investigated from the embryological standpoint.

#### MATERIAL AND METHODS

The material used in this investigation was obtained by request from Profs. H. F. Copeland and G. L. Stebbins of California in the year 1937. Fixations had been made by them in Bouin's and Nawaschin's fluids respectively. Soon after receipt the flower buds and carpels were run up through the alcohol-xylol series in the usual way and embedded in paraffin. Prof. H. F. Copeland sent, in addition, some material stored in bulk in 70% alcohol, which has been very useful in giving us an idea of the general morphology of the plant.

Due to other engagements and preoccupations the work could not be undertaken until very recently. Our account is not as complete as we would have liked it to be, but since there is no near prospect of getting further material, we have thought it worth while to publish such results as we have already obtained.

The sections were cut at a thickness of 6–16 microns, the thinner sections being more useful for a study of the male gametophyte and the thicker for the female gametophyte and embryogeny. Both iron-haematoxylin and safranin-fast green were used for staining. In the former case about five minutes in the mordant and five in the stain proved to be sufficient.<sup>2</sup>

For comparison we also cut some sections of *Damasodonum alisma*, *Eliasma natans* and *Echinodorus macrophyllus*, embedded material of which was supplied by Dr. H. Stenar of Sweden. In addition, Dr. B. M. Johri placed at our disposal some of his previously prepared slides of *Lemnophyton*, *Sagittaria*, and *Alisma*.

#### THE FLOWER

The flowers are bisexual<sup>3</sup> and actinomorphic. The perianth comprises two whorls. The outer consists of three persistent sepals which are usually imbricate but sometimes

<sup>1</sup> For a drawing of the entire plant, formerly called *Damasodonum californicum* Small, see Hutchinson (1934, p. 33).

<sup>2</sup> Such short timings have also yielded good results with other Alismaceae. Thus, Johri (1935a, p. 51) reports that in the hot weather at Agra one minute's immersion in haematoxylin was sufficient for *Lemnophyton*.

<sup>3</sup> In some genera of this family the flowers may be unisexual or polygamous. Thus, carpels are entirely absent in the male flowers of *Lemnophyton* (Johri, 1935a). In the male flowers of *Sagittaria sagittifolia* and *S. guayanensis* (Johri, 1935, b and c) rudimentary carpels are present, in the former case they go through the first division of the megaspore mother cell and in the latter even up to the four-nucleate stage of the embryo sac, after which the pollen is shed and the flowers wither.

twisted. The inner whorl consists of three petals, also imbricate, but crumpled and caducous. There are six stamens with extrorse anthers, two opposite each sepal. The carpels, generally 7-11, are free for the most part but appear to be slightly connate at the base due to fusion with the tip of the floral axis around which they are placed. The fruit is a bunch of stellately spreading single-seeded achenes with persistent styles. Figs 1-3 represent cross-sections of a flower bud at three different levels, drawn to indicate the relation of the different organs to one another.



Figs 1-3 1's flower bud at different levels  $\times 17$

The sepals and the ovary wall show a large number of schizogenous ducts already reported in the vegetative organs of several plants of the family.

#### MICROSPOROGENESIS

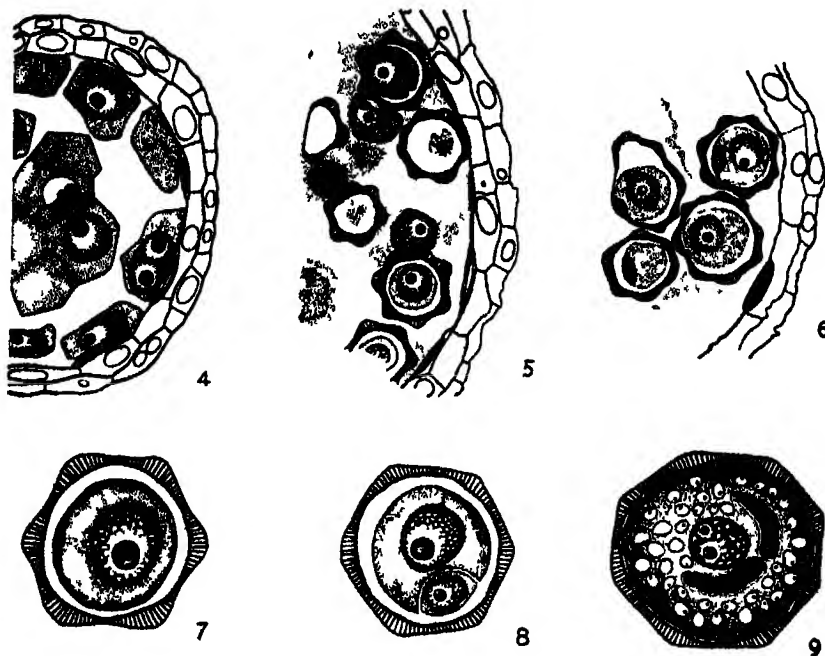
The development of the anther follows the usual course. The parietal tissue consists of an endothecium, a single ephemeral middle layer and the tapetum (fig. 4). The cells of the latter remain uninucleate and after reduction division in the pollen mother cells they become amoeboid and get into the loculus in the manner described for *Limnophyton* (Johri, 1935a) and other members of the family (see fig. 5). The plasmodial nuclei are as large as or slightly larger than the microspores when they have just separated from the tetrad. The periplasmodium begins to disappear after the generative cell has been cut off (fig. 6) and there is no trace of it when the sperm cells have been formed.

The middle layer becomes greatly flattened and crushed and is unrecognisable in the mature anther. The endothecium develops the usual fibrous thickenings which were very clearly seen in sections stained with safranin and fast green. In the oldest anthers, which were about to open, the epidermis was found to be shrivelled and almost unrecognisable, while the endothecium was very prominent.

#### MALE GAMETOPHYTE

The microspore mother cells go through the usual reduction divisions which are of the successive type and result in the formation of isobilateral tetrads. The microspores separate and become rounded, and the wall soon shows the differentiation into exine and intine. At first the nucleus lies in the middle which has a denser cytoplasm than the periphery (fig. 7), but it soon moves towards one side and divides to form the tube and generative nuclei which are separated by a thin hyaline membrane (fig. 8). After a time, when the generative cell has moved into the interior of the pollen grain, its cytoplasm is hardly visible but a clear space is generally present around the nucleus.

The generative cell divides to give rise to two more or less crescent-shaped male cells (fig. 9) The cytoplasmic layer around the male nuclei is so thin as to escape notice in



FIGS 4-9

Fig 4 Ts portion of anther to show the epidermis, endothecium, degenerating middle layer, uninucleate tapetum, and microspore mother cells  $\times 410$  Fig 5 Same, more advanced stage, showing microspores and tapetal periplasm  $\times 410$  Fig 6 Older stage, showing two celled pollen grains and disappearing periplasm  $\times 410$  Figs 7-9 Stages in the development of the male gametophyte Note the presence of starch grains in the mature pollen grain  $\times 800$

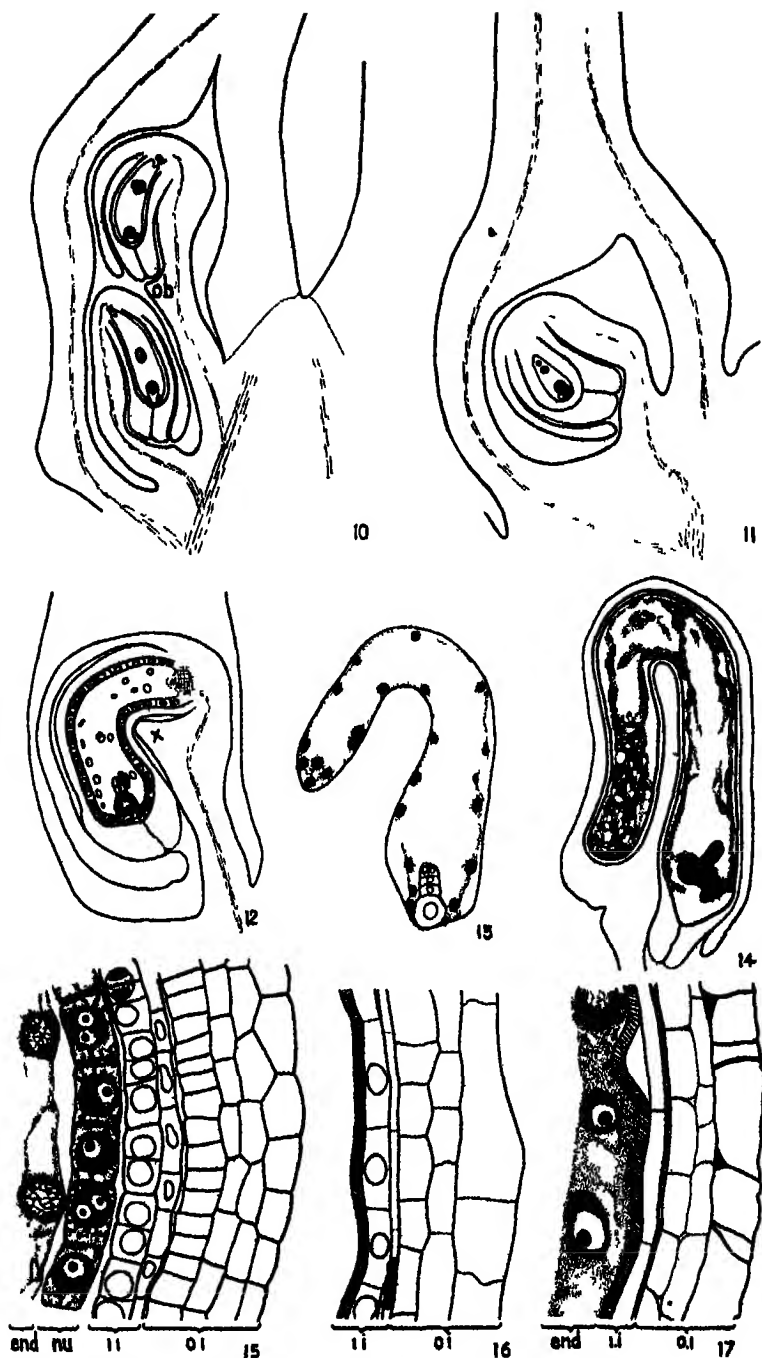
all but the most favourable preparations. Observations on the structure of the male cells are also rendered difficult because of the presence of large quantities of starch grains in the vegetative cytoplasm of the mature pollen grains. The germ pores are larger than is usual in the family (see also Wodehouse, 1936).

It is worthy of note that although the cytoplasm of the young pollen grain (microspore stage) is vacuolated, the vacuoles gradually disappear and are hardly visible at the time when the male gametes have been formed. This is in accordance with the observations of Schnarf (1937) who, after examining acetocarmine preparations of a large number of families, concludes that at the shedding stage the pollen grains are always devoid of any conspicuous vacuoles.<sup>1</sup>

#### THE OVULE

There is a single anatropous ovule in each carpel. In *Damasonium alisma* there are two ovules, oriented as shown in fig 10. If the lower of these were to disappear, we would

<sup>1</sup> Previous authors, viz., Dahlgren (1928, fig. 86) in *Alisma natans*, Narasimha Murthy (1933, fig. 33) and Johri (1935a, fig. 39) in *Limnophyton*, Johri (1935b, figs. 1 and 2) in *Sagittaria sagittifolia*, Johri (1935c, figs. 11 and 52) in *S. guayanensis* and *S. latifolia*, show large vacuoles in the mature pollen grains. On a re-examination of Dr. Johri's preparations we find that the vacuolar appearance is really due to the presence of starch grains which often remain unstained with haematoxylin. On suitably restaining the slides and in some cases even without doing so we were able to observe the hilum in the centre of each such space. The iodine test also yielded positive results, thus confirming the presence of starch.



Figs. 10-17

Fig 10. L.s. carpel of *Damaecium alisma* at fertilisation stage. Note the orientation of the ovules and the obturator (ob)  $\times 46$ . Fig 11 L.s. carpel of *Machaerocarpus* at mature embryo sac stage  $\times 46$  Fig 12 L.s. ovule showing 3-celled embryo and persistent nucellar epidermis. Note beginning of curvature of the ovule due to a multiplication of the cells of the funiculus at place marked  $\times$   $\times 54$  Fig 13 Embryo sac showing young embryo and free endosperm nuclei.  $\times 56$  Fig 14. L.s. ovule with older embryo  $\times 27$  Fig 15 L.s. portion of ovule shortly after fertilization showing detail of outer integument (o.i.), inner integument (i.i.), single layer of nucellus cells (nu.), and free nuclear endosperm (end)  $\times 340$ . Fig. 16. L.s. ovule showing the condition of integuments at a slightly older stage. Note that the outer layer of the inner integument has become considerably flattened and crushed and the inner layer has been outlined on its inner side.  $\times 338$  Fig. 17. Still older stage showing a thickening of the outer layer of the outer integument and a virtual disappearance of the outer layer of the inner integument.  $\times 338$ .

get a condition similar to that in *Machaerocarpus*, *Alisma*, *Ethema*, *Limnophyton* and *Sagittaria*<sup>1</sup> also have a single ovule per carpel.

The nucellus is not massive, being only two-layered for the most part<sup>2</sup>. The inner layer begins to dissolve when the embryo sac is mature but the epidermis persists during the earlier stages in embryogeny, and, owing to the dense cytoplasm and prominent nuclei of its cells, it gives the appearance of an integumentary tapetum (figs 12, 15). It is the cells at the micropylar end which hold on for the longest time.

There are two integuments, of which the outer is mostly three to four-layered and the inner two-layered (fig 15), but its micropylar portion is thicker. After the nucellus disorganises the inner layer of the inner integument comes in direct contact with the embryo sac. Its cells undergo a number of radial divisions to keep pace with the elongation of the embryo sac and become richly protoplasmic. Later its inner tangential wall becomes greatly thickened and cutinised and forms a protective lining to the tissues within it (figs 16, 17). The outer layer, on the other hand, becomes stretched and crushed to a mere streak. The outer integument does not undergo much change beyond a little elongation and flattening of its cells and the thickening of its outer walls (fig 17).

After the embryo sac is fertilised, the cells of the funiculus begin to divide actively at the place marked x in fig 12, so that there is a swelling of the tissue in this region, and in later stages the embryo sac becomes doubled upon itself (figs 13, 14).

In *Damasomum* (Dahlgren, 1928) there is an obturator-like swelling on the funiculus but we did not find it in *Machaerocarpus* (compare figs 10 and 11).

#### MEGASPOROGENESIS AND DEVELOPMENT OF THE EMBRYO SAC.

The stages in the development of the embryo sac are shown in figs 18 to 25. The primary archesporial cell (fig 18) functions directly as the megaspore mother cell (fig 19). No wall cells are cut off but certain cells of the nucellar epidermis occasionally undergo a periclinal division as also noted in some other plants of the family<sup>3</sup>.

Of the two dyad cells formed after the first division of the megaspore mother cell, the lower enlarges and functions while the upper promptly degenerates and is reduced to a darkly staining cap on the former. This resembles the condition in the other plants of the family as far as they have been investigated<sup>4</sup>.

The first division in the lower dyad cell (fig 20) gives rise to two nuclei which move apart to the poles, a large vacuole appearing in the centre (fig 22). In some cases a delicate wall appears after the division (fig 21) but it soon disappears and was never seen in older stages<sup>5</sup>.

The two-nucleate stage is followed by the four-nucleate (fig. 23). The micropylar end of the embryo sac is now broader than the chalazal. The two chalazal nuclei are also smaller than the micropylar, the lowest being the smallest and having a degenerated appearance from the very beginning<sup>6</sup>.

<sup>1</sup> In *Sagittaria sagittifolia* (Johri, 1935b) an additional ovule was seen in one case, which was however much arrested in its development.

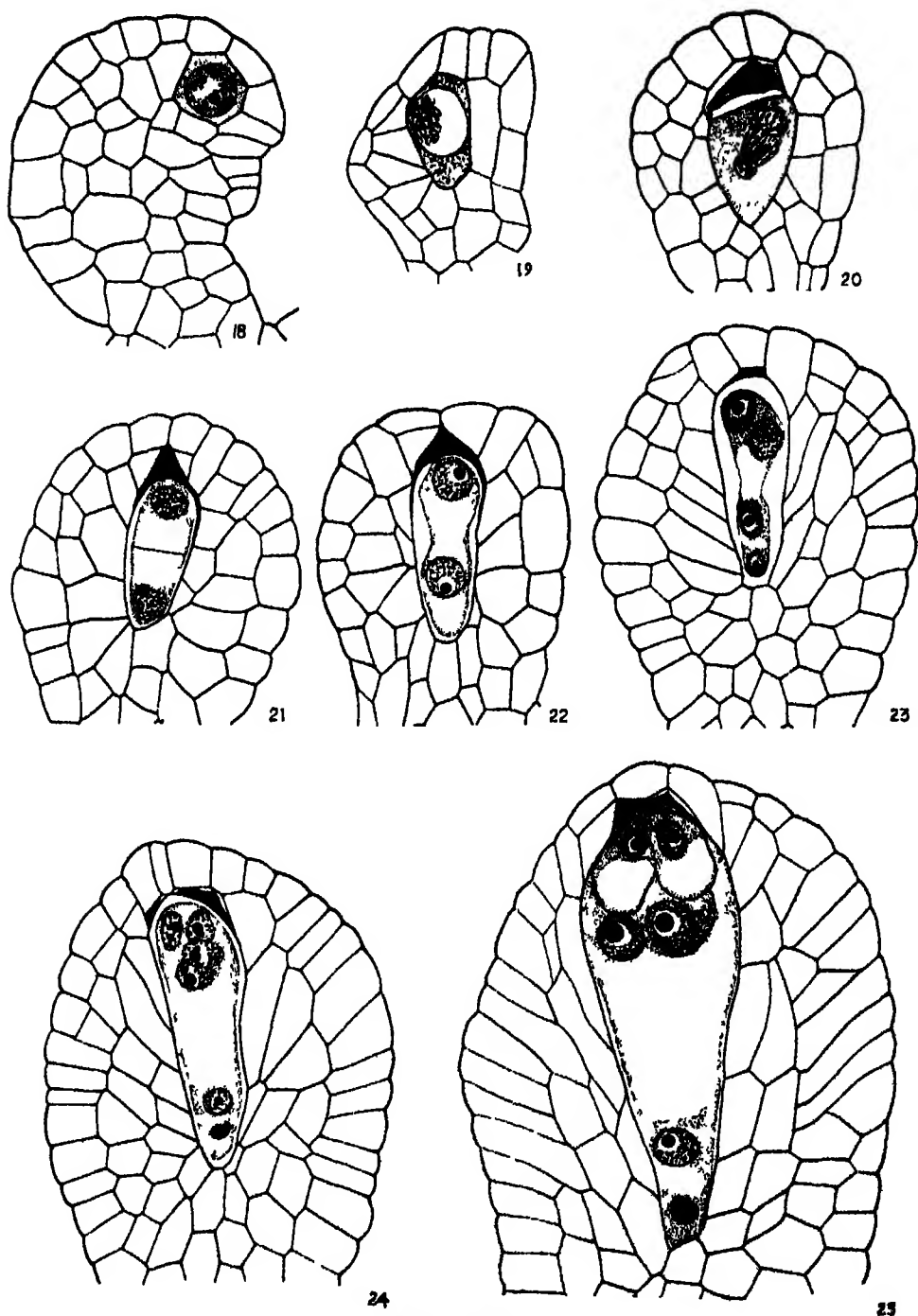
<sup>2</sup> There is no uniformity in the family regarding the number of cell layers composing the nucellus. In *Damasomum alisma*, *Alisma plantago* (Dahlgren, 1928) and *Alisma plantago-aquatica* (Johri, 1936a) the nucellus is already on the way to disorganisation and disappearance at the time of fertilisation. In *Machaerocarpus*, as noted above, the nucellar epidermis persists for a longer time. Narasimha Murthy's (1933) figs 35 and 36 seem to indicate that in *Limnophyton* the nucellus is lost at the 2-nucleate stage of the embryo sac but this is obviously incorrect as pointed out by Johri (1935a). Actually the nucellus seems to persist even longer in *Limnophyton* than in *Machaerocarpus*.

<sup>3</sup> See Johri (1935a) on *Limnophyton*, fig 46.

<sup>4</sup> Narasimha Murthy (1933, p. 10) says that the megaspore mother cell gives rise to two 'megaspores' of which the chalazal develops further. These are really the dyad cells (for terminology see Maheshwari, 1937, p. 1 and 1941, p. 230).

<sup>5</sup> A similar membrane has been reported in some plants of the family Butomaceae, viz., *Butomopsis lanceolata* (Johri, 1936b), *Limnocharis emarginata* (Johri, 1938a) and *Hydrocleis nymphoides* (Johri, 1938b), and suggests the derivation of the bisporic type of embryo sac from the monosporic. In the latter this wall is permanent.

<sup>6</sup> In *Limnophyton*, *Sagittaria* and *Alisma*, Johri (1935 a, b, c, and 1936a) reports that the chalazal nucleus occasionally fragments into two or three nuclei. We could find only one such instance in



Figs 18-26.

Fig 18. L's young ovule showing hypodermal archesporial cell  $\times 428$ . Fig 19. Megaspore mother cell in synizesis.  $\times 428$ . Fig 20. Lower dyad cell dividing  $\times 428$ . Fig 21. Two-nucleate embryo sac. Note the thin membrane at the centre  $\times 428$ . Fig 22. Two-nucleate embryo sac older than in fig 21.  $\times 428$ . Fig 23. Four-nucleate embryo sac.  $\times 428$ . Fig 24. Six nucleate embryo sac.  $\times 428$ . Fig 25. Fully organized embryo sac showing two synergids, an egg-cell, an upper polar nucleus, a lower polar nucleus and a single antipodal nucleus.  $\times 428$ .

Only the two micropylar nuclei divide again giving rise to a quartet, which produces the egg apparatus and the upper polar nucleus. The lower polar nucleus is contributed from the chalazal end and the remaining nucleus may be said to represent the solitary 'antipodal' (figs 24 and 25).

#### FERTILISATION

Fig 25 shows an embryo sac just prior to fertilisation. The egg apparatus consists of two hooked synergids<sup>1</sup> and a prominent egg-cell, the two polar nuclei have not yet met and there is a single antipodal nucleus. Double fertilisation takes place normally (fig 26). The pollen tube destroys one of the synergids and the other disappears some time afterwards. Johri (1936b) states that in *Butomopsis lanceolata*,<sup>2</sup> belonging to the family Butomaceae, and *Sagittaria sagittifolia* (Johri, 1935b) syngamy may take place a little later than triple fusion, while Narasimha Murthy (1933) claims that in *Limnophyton* triple fusion is a very slow process as compared to syngamy. The situation in *Machaerocarpus* seems to resemble the latter in that the second sperm nucleus can be distinguished for some time after the first one has already merged itself within the egg.

#### ENDOSPERM

The early stages in endosperm formation were difficult to investigate since the nucellar cells adjacent to the embryo sac begin to disorganise and their nuclei, which now float freely in the cytoplasm of the embryo sac, become mixed up with the endosperm nuclei and are difficult to distinguish from them. The nucellar nuclei may even increase in volume after becoming liberated into the embryo sac and their behaviour recalls that of the jacket nuclei of the archegonia of some gymnosperms.<sup>3</sup>

Unlike *Echinodorus* (Dahlgren, 1928), *Limnophyton* (Johri, 1935a) and *Sagittaria* (Johri, 1935 b, c and 1936a) the first division of the primary endosperm nucleus is not followed by a chambering of the embryo sac into two portions. Free nuclear divisions continue for a long time (fig 14) and wall formation either does not occur at all or takes place only at the periphery and in much older stages.<sup>4</sup> A free nuclear endosperm is also seen in *Alisma*, *Damasorum* and *Elisma* (Dahlgren, 1928).

#### EMBRYO

The fertilised egg divides after the primary endosperm nucleus has undergone one or two divisions. This is in accordance with the observations of other authors. Only Narasimha Murthy<sup>5</sup> (1933) reports that in *Limnophyton* the fertilised egg is precocious in its development and divides without passing through any resting period.

*Machaerocarpus* and consider it to be very rare in this plant. In *Limnophyton* (according to Narasimha Murthy, 1933 and 1935a) the embryo sacs are originally eight nucleate but may later become six nucleate owing to a degeneration of two of the chalazal nuclei. We have re-examined several slides prepared by Dr. Johri and fully support his statement that the embryo sacs are primarily six-nucleate due to a failure of division of the two chalazal nuclei of the four-nucleate stage. When more than six nuclei occur, they are due to a fragmentation or amitotic division of the lowest chalazal nucleus.

<sup>1</sup> Hooked synergids have been recorded in recent years in other plants of the families Alismaceae and Butomaceae, for a complete list see Dahlgren (1928, p. 225).

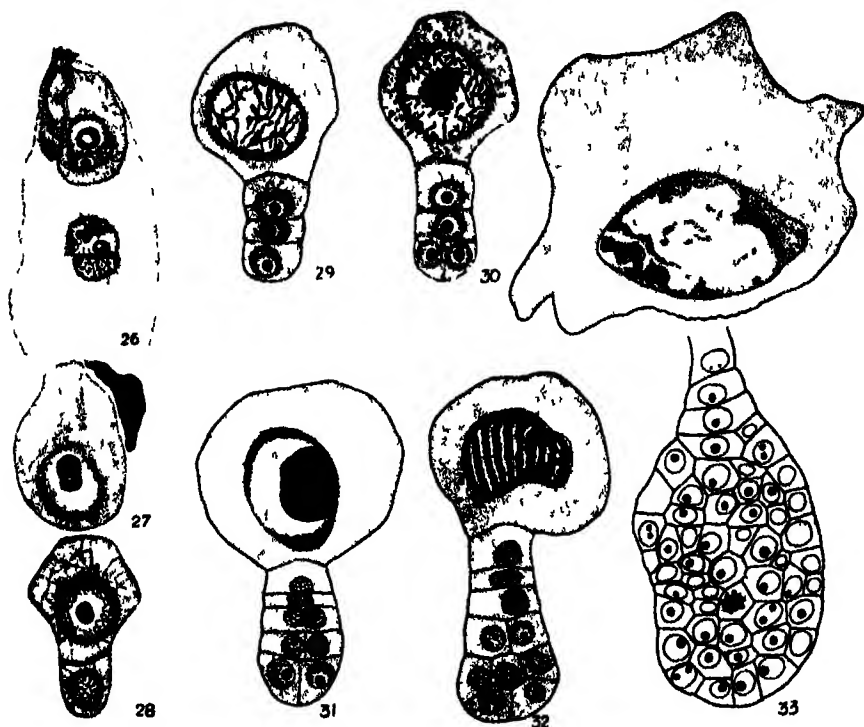
<sup>2</sup> The present name of this plant is *Tenagocharia latifolia* Buchen.

<sup>3</sup> The entry of nucellar nuclei into the embryo sac and the interference caused by them misled Campbell (1910, 1911) to describe a many-nucleate embryo sac in *Pandanus* which remained a puzzle until quite recently. Fagerlin (1940) has now cleared the situation and demonstrated that the embryo sac of *Pandanus* develops quite normally but the nuclei of the adjacent cells become incorporated into it, increase in number, and even take part in the formation of the primary endosperm nucleus which shows different degrees of polyploidy depending not only upon the number of nuclei that have fused to form it but also on the proportion of haploid and diploid nuclei amongst them.

<sup>4</sup> We were unable to ascertain this point definitely since sufficiently old material was not available to us.

<sup>5</sup> He writes (1933, p. 11) that in *Limnophyton obtusifolium* triple fusion 'usually takes place when the embryo is in a two-celled stage', which would obviously mean that the zygote divides before the primary endosperm nucleus. We are unable to confirm this from our study of Dr. Johri's slides of the same plant. We find the reverse to be the general condition. Of course stray cases are known in the Halobiales (see Dahlgren, 1928, on *Zostera*) and other plants when the embryo continues to grow while the fusion nucleus remains undivided, but these are exceptions rather than the rule.

The first division of the zygote (fig. 27) results in the formation of two superposed cells (fig. 28) of which the basal becomes large and vesicular and does not divide further. The



FIGS 26-33

Fig. 26. Part of embryo sac showing double fertilisation  $\times 308$  Fig. 27. Fertilised egg.  $\times 340$  Fig. 28. Two-celled proembryo  $\times 256$  Fig. 29. Four celled proembryo  $\times 240$  Figs. 30-33. Further stages in the development of the embryo. Note the large basal cell. Fig. 30  $\times 256$  and rest  $\times 240$

second produces a row of three cells (fig. 29) of which the terminal divides longitudinally to form quadrants (fig. 30) and octants. Due to lack of material we were unable to trace the further development of the embryo with any thoroughness but stages like those in figs 31 to 33, which we came across, give the impression that it does not differ materially from *Sagittaria*, which has been so thoroughly described by Souèges (1931), and *Damasonium* (Lemesle, 1929).

#### THEORETICAL CONSIDERATIONS

The main embryological characters of the family Alismaceae may be summarised as follows. Comparisons have also been made with other families of the order Helobiales in order to help in arriving at some conclusions as to its relationships —

*Development of the anther and microsporogenesis.*—Detailed information is available only about certain plants of the family. *Limnophyton obtusifolium* (Narasimha Murthy, 1933, Johri, 1935a), *Sagittaria guayanensis* (Johri, 1935c) and to some extent *Machaerocarpus*.

There are three parietal layers—the endothecium, middle layer and tapetum. The cells of the latter remain uninucleate and become amoeboid. All the other families of the order Helobiales also show an essentially similar type of periplasmodium formation, leaving only the Najadaceae about which the requisite information is lacking.

The divisions of the microspore mother cells are successive and result in tetrads of the isobilateral type. Only in some species of *Aponogeton* (Aponogetonaceae) the divisions are simultaneous (Sane, 1939). In *Butomopsis* (Johri, 1936b) and *Ottelia* (Narasimha Murthy, 1935) some irregular types of tetrads have also been noticed. In *Halophila ovata* (Kausik and Rao, 1942) and *Cymodocea isoetifolia* (Rao, 1941), belonging to the Hydrocharitaceae and Potamogetonaceae respectively, the microspore mother cells are elongated and divide transversely to give rise to linear tetrads. *Zostera* (Potamogetonaceae) is also peculiar (Rosenberg, 1901a), but its pollen grains do not appear to have received further attention for more than forty years.

**Male gametophyte**—The pollen grains in the Alismaceae are uniformly trinucleate. As noted in the present investigation they are often filled with large quantities of starch grains and the thin layer of cytoplasm around the male nuclei is therefore liable to be obscured.

The three-nucleate condition of the pollen is of universal occurrence in the Helobiales, the only exceptions being *Ottelia alismoides* (Narasimha Murthy, 1935b), *Triglochin palustris* (Wulff, 1939), *Lilaea subulata* (Campbell, 1898) and *Zannichellia palustris* (Campbell, 1897). Of these the last two deserve reinvestigation.

**Ovule**—In the entire order the ovules are bi-integumented. The archesporial cell cuts off a wall cell in all the families (with few exceptions) except the Alismaceae and most of the Butomaceae<sup>1</sup>. In the latter, *Limncharis*, *Hydrocleis* and *Butomopsis* have no wall cell while *Butomus* usually has it but sometimes it may also be without it.

**Megasporogenesis and development of the embryo sac**—All the recently investigated plants of the family, comprising seven genera (*Alisma*, *Damasonium*, *Echinodorus*, *Elisma*, *Limnophyton*, *Machaerocarpus* and *Sagittaria*) and more than fifteen species, have the bisporic *Allium*-type of embryo sac, in which the lower dyad functions. In the allied family Butomaceae also, three genera [*Butomopsis*, *Limncharis* and *Hydrocleis* (Johri, 1936b, 1938a, 1938b)] have bisporic embryo sacs and only *Butomus* (Holmgren, 1913) is monosporic. This is in sharp contrast with the condition in the other families of the order in which a monosporic eight-nucleate embryo sac is of general occurrence.

**Embryo sac**—In most of the Alismaceae studied so far, the embryo sac is six-nucleate, and as a result the micropylar portion of the embryo sac is organised as usual but there are only two nuclei in the chalazal portion, the lower polar and the single 'antipodal'. In *Echinodorus runcunculoides* (Dahlgren, 1928) and *E. macrophyllus* (Dahlgren, 1934) reduction has proceeded still further so that even the primary chalazal nucleus of the two-nucleate stage fails to divide further and the resulting embryo sac is only five-nucleate without any lower polar nucleus and with a single antipodal.

Here also Butomaceae is the only family which offers comparison. Out of the four genera, which have been investigated, *Butomopsis*, *Limncharis* and *Hydrocleis* are essentially similar to the alismads, *Butomus* alone having a normal eight-nucleate embryo sac with three antipodal cells.

**Endosperm**—There are two distinct modes of endosperm formation in the Alismaceae. *Echinodorus*, *Limnophyton* and *Sagittaria* belong to the Helobiales-type, while *Alisma*, *Damasonium*, *Elisma* and *Machaerocarpus* belong to the Nuclear-type. The only other family of the order, which shows both types of endosperm development, is Scheuchzeriaceae, having the Nuclear-type in *Triglochin* and *Lilaea* and the Helobiales-type in *Scheuchzeria* (for full references see Stenar, 1935). In Potamogetonaceae, *Zostera* is exceptional in having a nuclear endosperm, this was long doubted but Rosenberg's work (1901b) has now been fully confirmed by Dahlgren (1939). A comparative study of the illustrations given by these authors seems to show that the Nuclear-type is associated with an embryo sac having a comparatively broader base, while the embryo sacs of plants with the Helobiales-type have a more narrow and tapering chalazal end.

**Embryo**—The development of the embryo has not been very thoroughly studied in all the families but the available facts seem to indicate that the *Sagittaria*-type with its

<sup>1</sup> Kausik's (1940, p. 87) statement that 'the formation of a parietal cell is characteristic of all the Helobiales' is obviously incorrect. This is not true of the Alismaceae and most of the Butomaceae, nor of *Zostera* (Dahlgren, 1939) belonging to the Potamogetonaceae.

prominent undivided basal cell is of wide occurrence in the entire order. The endosperm becomes used up by the time the embryo is mature. In the Alismaceae and most of the Butomaceae the embryo is curved like a horseshoe.

**Conclusion**—The available information on the embryology of the Helobiales indicates that although the Alismaceae and the Butomaceae show close similarities with the other families of the order, they have a more intimate relationship with each other than with any of the other families. The character of their pollen grains (for details see Wodehouse, 1936), the absence of a wall cell in the ovule, the presence of a bisporic six or five-nucleate embryo sac, their horseshoe-shaped embryo and their more or less free carpels, all seem to warrant the creation of a separate order Alismatales for their reception.<sup>1</sup> In any case, Markgraf's (1936) grouping of the Butomaceae and the Hydrocharitaceae into the order Butomineae and the placing apart of the Alismaceae into another suborder Alismatineae can hardly be justified on embryological grounds. We are also not in agreement with Hutchinson's idea of splitting the Helobiales into several separate orders, viz., Alismatales, Butomales, Aponogetonales, Potamogetonales and Najadales, since this appears to under-rate the many close and obvious resemblances between some of the families included under them.

Hutchinson and some other botanists have also laid great stress on the primitiveness of the Butomaceae and Alismaceae and their resemblances with the Nymphaeaceae and Ranunculaceae, chiefly on the basis of the structure of the gynaecium. It is even stated that except for its solitary cotyledon and lack of endosperm, the genus *Ranalisma* might equally well be placed in the Ranunculaceae. This may appear to be so superficially but the great gap between the morphological and embryological characters of the Ranunculaceae and Alismaceae precludes the probability of any close relationship between them (see also Eber, 1934). Our efforts to obtain material of *Ranalisma* have so far been unsuccessful and definite opinion on this point must therefore await the investigation of this critical genus.

#### ACKNOWLEDGEMENTS

In conclusion, we wish to record our grateful thanks to Profs. H. F. Copeland and G. L. Stebbins for providing the material on which this study is based, to Dr. H. Stenar (Sweden) for very kindly sending us some paraffin material of *Damasodonum*, *Elisma* and *Echinodorus* which was cut for comparison, and to Dr. B. M. Johri (Agra) for the loan of his slides of the Alismaceae and Butomaceae. Mr. A. K. Chakravarti, who was a colleague for some weeks in this Department, very kindly prepared the originals of figs. 13, 15, 19, 26, 27, 28 and 30, and would have been a co-author of this paper but for his sudden departure from Dacca to take up another appointment.

#### SUMMARY

1. In *Machaerocarpus californicus* the flowers are bisexual and actinomorphic, with three persistent sepals, three petals, six stamens and seven to eleven carpels which give rise to a bunch of stellately spreading achenes.

2. The parietal tissue in the anther consists of a well-developed endothecium, an ephemeral middle layer and the tapetum. The cells of the latter remain uninucleate and form a periplasmodium.

3. The pollen grains are tri-nucleate with a vegetative nucleus and two male cells. The vegetative cytoplasm is full of starch grains.

4. There is a single anatropous ovule in each carpel. In later stages the lateral cells of the funiculus divide actively so that the ovule becomes bent like a horseshoe. Of the two cell layers which form the inner integument, the outer disorganises and the inner tangential wall of the other becomes heavily cutinised to give protection to the embryo.

5. The hypodermal archesporial cell functions directly as the megaspore mother cell without cutting off any wall cell. Of the two dyad cells, formed after the first division,

<sup>1</sup> This view seems to find support from Rendle (1930), who includes the Butomoidae and Alismoidae under a single family Alismaceae.

the lower functions to give rise to a six-nucleate embryo sac. The development is therefore a modification of the *Allium*-type, showing reduction in the chalazal part of the sac.

6 The mature embryo sac consists of an egg-cell, two hooked synergids, an upper polar nucleus, a lower polar nucleus and a single antipodal nucleus.

7 Double fertilisation occurs normally. The endosperm is free nuclear and the embryo is of the *Sagittaria*-type.

8 From a comparison of the embryological characters of the Alismaceae with those of other families of the Helobiales, it appears that its closest relationship is with the Butomaceae, and it would be appropriate to create a separate order Alismatales for their reception.

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# THE EFFECT OF SCREENING ON THE BREMSSTRAHLUNG AND PAIR-CREATION PROCESS AND ITS CONSEQUENCE ON THE CASCADE THEORY

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## ABSTRACT

Considering an empirical formula for the function  $\phi_1(\rho)$  occurring in the expression for the cross-sections of the pair-creation and Bremsstrahlung processes, expressions for these cross-sections have been obtained which allow for the incompleteness of screening to a sufficient degree of accuracy, particularly in the region where this is important for the calculations of the Cascade Theory. Using these cross-sections results have been obtained which give the number of cascade electrons and positrons in different materials at any depth below the top and also the energy spectra of such particles. The results show the dependence of the cascade on the nature of the material in which the shower is produced. It appears that the maximum of the shower transition curve is shifted to greater depths in heavier materials. The results obtained show that the approximations made in assuming that the screening is always complete for the calculations of the cascade theory will not produce any appreciable error in lighter materials, such as air, but will produce some error in heavier materials such as Pb, which again is not very large.

It has been mentioned by several authors that the screening of the atomic potential by the outer electrons would have a considerable effect on the cross-sections for the radiation and pair creation phenomena, because a large part of these processes takes place at large distances from the nucleus of the field-producing atom, i.e. at places where the field is no longer Coulombian.

Assuming a Fermi model for the distribution of atomic electrons, Bethe and Heitler (1934) have calculated the form of the cross-sections. The effective differential cross-sections for the emission by an electron of energy  $E$  of a quantum of energy lying between  $E'$  and  $E' + dE'$  while passing through the field of an atom of nuclear charge  $Ze$  is given by,

$$\frac{4Z^2}{137} \left( \frac{e^2}{mc^2} \right)^2 \log(183Z^{-1/2}) R(E, E') \frac{E' dE'}{E^2}, \quad \dots (1)$$

where

$$R(E, E') = \left[ 1 - \frac{4}{3} \frac{E}{E'} + \frac{4}{3} \frac{E^2}{E'^2} \right] (\chi_1 + \chi_2) - \chi_2 \quad \dots (2)$$

and

$$\chi_1 = \frac{\phi_1(\rho) + 4 \log Z^{-1/2}}{4 \log(183Z^{-1/2})}; \quad \chi_2 = \frac{\phi_1(\rho) - \phi_2(\rho)}{8 \log(183Z^{-1/2})} \quad \dots (3)$$

with

$$\rho = \frac{100}{Z^{1/2}} \left| \frac{mc^2 E'}{E(E - E')} \right| \quad \dots (4)$$

where  $\phi_1(\rho)$  and  $\phi_2(\rho)$  are functions of  $\rho$  only. Since these functions depend on a general atomic form-factor, which is known only numerically (Bethe, 1930), analytic expressions for  $\phi_1(\rho)$  and  $\phi_2(\rho)$  in a closed form cannot be obtained, although they are given numerically by Bethe and Heitler. When the screening is complete,  $\rho$  tends to zero and then  $\chi_1 = 1$

and  $\chi_2 = 1/12 \log(183Z^{-1/3})$ . In a previous paper Bhabha and the present author (1943),\* while developing the Cascade Theory, have assumed for simplicity that  $\rho = 0$  always, whatever the values of  $E'$  and  $E$  may be. This will certainly introduce some error, which will be larger for heavier material since the radiation and pair creation processes continue to be the dominating ones in heavier materials at much lower energies where the actual cross-sections differ largely from those for the case of complete screening. We have discussed in the previous paper, to what extent the final result will be in error due to this approximation purely from the physical nature of the problem. It is the purpose of the present paper to study this deviation analytically as far as possible in order to get the results of the Cascade Theory more accurately, particularly for heavier elements. The function  $R(E, E')$  is not only a function of the ratio  $E'/E$ , but is also a function of  $E/mc^2$ . But for simplicity and mathematical tractability, we have in previous papers replaced  $R(E, E')$  by  $R_0(E, E')$  to which  $R(E, E')$  reduces in the case of complete screening. In that case  $R_0(E, E')$  is purely a function of  $E'/E$  and the cascade problem can be solved exactly as has been done in the previous papers (Bhabha and Chakrabarty, 1942)†

The expression for  $R(E, E')$  can be written in the form,

$$R(E, E') = \left[ 1 - \left( \frac{4}{3} + \alpha \right) \left\{ \frac{E}{E'} - \frac{E^2}{E'^2} \right\} \right] \frac{\phi_1(\rho) + 4 \log Z^{-1/3}}{4 \log(183Z^{-1/3})} \quad \dots \quad (5)$$

where

$$\alpha = \frac{2}{3} \frac{\phi_1(\rho) - \phi_2(\rho)}{\phi_1(\rho) + 4 \log Z^{-1/3}}$$

So that

$$R(E, E') = R_0(E, E') \left[ \{ \phi_1(\rho) + 4 \log Z^{-1/3} \} / 4 \log(183Z^{-1/3}) \right] \quad \dots \quad (6)$$

where

$$R_0(E, E') = 1 - \left( \frac{4}{3} + \alpha \right) \left( \frac{E}{E'} - \frac{E^2}{E'^2} \right) \quad \dots \quad (6a)$$

$\alpha$  can be safely neglected, since for all elements it is very small, but in order to compare the results with those of the previous papers, where it has been retained, we have also retained it here and have treated it to be a very small constant ( $\approx 0.025$ ), neglecting its variation with  $Z$  and  $\rho$ .

From the graphical representation of  $\phi_1(\rho)$  as given by Bethe and Heitler, it is clear that to a very good approximation  $\phi_1(\rho)$  can be represented by the following equation

$$\phi_1(\rho) = 4 \log(183) - 4\rho + a\rho^2 \quad \dots \quad (7)$$

where  $a \approx 70$ . It may be noted here that the introduction of higher powers of  $\rho$  namely  $\rho^3, \rho^4, \dots$  in (7) may give a much closer approximation, but the following analysis will show that the effects of such terms are unimportant in the calculations of the Cascade Theory.

In the case of the bremsstrahlung process  $\rho$  is given by

$$\rho = \frac{100mc^2}{Z^{1/3}} \frac{E'}{E(E'-E')} = \frac{200mc^2}{\beta Z^{1/3}} \frac{\beta}{2E} \left[ \frac{E'}{E} + \frac{E'^2}{E^2} + \dots \right] \quad \dots \quad (8a)$$

and for the process of pair creation we have

$$\begin{aligned} \rho &= \frac{100mc^2}{Z^{1/3}} \frac{E}{E'(E-E')} \\ &= \frac{200mc^2}{\beta Z^{1/3}} \frac{\beta}{2E} \left[ 3 + \left( \frac{E'}{E} \right)^2 + \left( 1 - \frac{E'}{E} \right)^2 + \dots \right] \quad \dots \quad (8b) \end{aligned}$$

\* To be referred to in this paper as A.

† To be referred to in this paper as B.

But for different materials (i.e. for different values of  $Z$ )

$$4 \left( \frac{200mc^2}{\beta Z^{1/3}} \right) \frac{82}{Z} \approx 4 \log (183Z^{-1/3})$$

as will be apparent from the following table in which the value of

$$\frac{200mc^2}{\beta Z^{1/3}} \frac{82}{Z} \left[ \log (183Z^{-1/3}) \right]^{-1} = P \text{ (say)}$$

is given for different materials

TABLE I

	Au	H <sub>2</sub> O	Al	Fe	Pb
P	1.10	1.10	1.16	1.04	0.93

It may be noted here that  $\beta Z$  is not completely independent of  $Z$  but varies slightly with the material

Substituting these values of  $\rho$  and simplifying we see that the cross-sections  $\pi(E, E')dE'$  and  $\gamma(E, E')dE'$  for the processes of Bremsstrahlung and pair creation are given by

$$\begin{aligned} \pi(E, E')dE' = A R_0(E, E') \frac{E'dE'}{E^2} & \left[ 1 - \frac{Z}{82} \frac{\beta}{2E} \left( \frac{E'}{E} + \frac{E'^2}{E^2} \right) \right. \\ & \left. + \frac{Z}{82} \frac{a}{4} \left( \frac{200mc^2}{\beta Z^{1/3}} \right) \left\{ \frac{\beta}{2E} \left( \frac{E'}{E} + \frac{E'^2}{E^2} \right) \right\}^2 \right] \end{aligned} \quad (9a)$$

$$\begin{aligned} \gamma(E, E')dE' = A R_0(E', E) \frac{dE'}{E} & \left[ 1 - \frac{Z}{82} \frac{\beta}{2E} \left\{ 3 + \frac{E'^2}{E^2} + \left( 1 - \frac{E'}{E} \right)^2 \right\} \right. \\ & \left. + \frac{Z}{82} \frac{a}{4} \left( \frac{200mc^2}{\beta Z^{1/3}} \right) \left\{ \frac{\beta}{2E} \left( 3 + \frac{E'^2}{E^2} + \left( 1 - \frac{E'}{E} \right)^2 \right) \right\}^2 \right] \end{aligned} \quad (9b)$$

where

$$A = \frac{4Z^2}{137} \left( \frac{e^2}{mc^2} \right)^2 \log (183Z^{-1/3}) = l^{-1} N^{-1}$$

and  $R_0(E, E')$  is the value of  $R(E, E')$  when the screening is complete and is given by (6a).

Only the first terms in square brackets of (9a) and (9b) were taken in A and B, to which the present expressions reduce when  $E \rightarrow \infty$ , i.e. in the case of complete screening. In equations (8) the powers of  $E'/E$  higher than  $(E'/E)^2$  have been neglected. The addition of further terms containing higher powers of  $(E'/E)$  or  $(1 - E'/E)$ , however, will slightly alter the values of  $a, b, c, d$  as given in (18) but their ultimate effect on the final result will be negligible as will appear from the next section. This is also justified since the case when  $E' \rightarrow E$ , is not important for the cascade process. Moreover in this region the expressions obtained by Bethe and Heitler are not valid, since they have used Born's approximation for the calculations which again is not valid when  $(E'/E) \rightarrow 1$ . It is also clear that although (9a) and (9b) differ from the expressions given by Bethe and Heitler in this region, its consequence on the Cascade Theory will be unimportant. The expressions for the cross-sections given by (9) have been plotted for some different values of  $E$ , together with the corresponding curves obtained from the Bethe and Heitler expression. In fig. 1, I have drawn the figures for Pb, but it can easily be seen that the fit for similar curves for lighter elements will be much better than that in the case of Pb. Fig. 1 shows

that the fit between the curves obtained from (9) and the corresponding Bethe-Heitler curves is quite good except in the region when  $(E'/E) \rightarrow 1$ , where, for reasons stated above, the Bethe-Heitler curves are doubtful and possibly the true curves will tend more towards that given by (9a) and (9b). To my knowledge no one has as yet treated the problem without using Born's approximation for the relativistic region, but Sommerfeld (1931) has discussed a similar problem for the non-relativistic region. The trend of his curves in the region where  $(E'/E) \rightarrow 1$  suggests that even in the relativistic region also, the curves will tend to a finite limit instead of tending to zero and will probably approach more towards the expression given by (9). This has also been suggested by Bethe and Heitler. The two sets of curves as drawn in Figs 1a and 1b differ appreciably when  $\rho$  is not small. For that region the higher powers of  $\rho$  should be introduced in (7) and also the higher

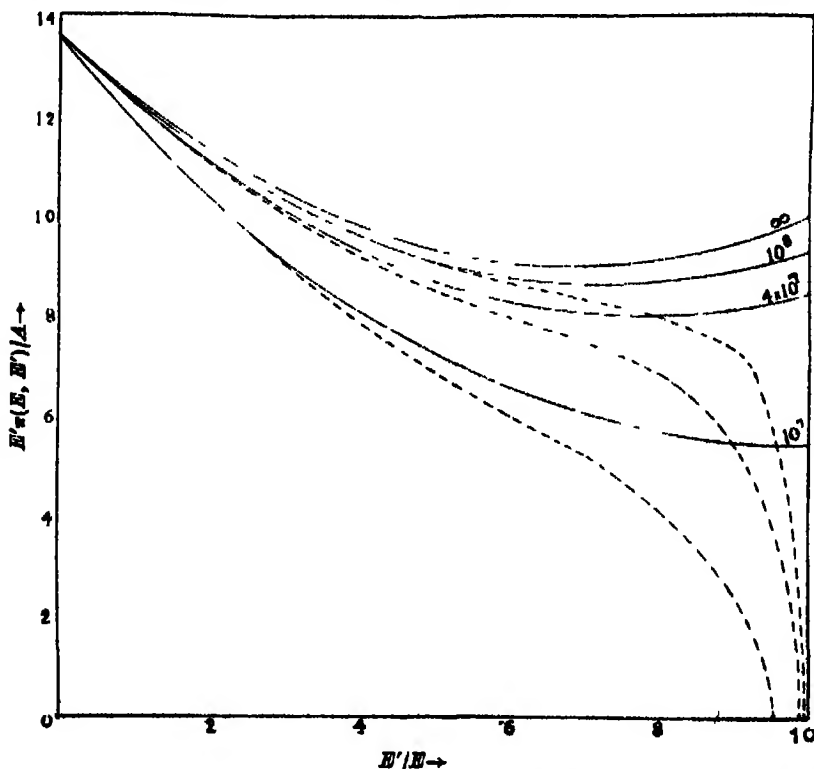


FIG. 1(a) Differential radiation probability per radiation length of Pb for electrons of various energies. The numbers attached to the curves indicate the energy  $E$  of the primary particle. Solid lines correspond to equation (9a) and the dotted lines represents Bethe-Heitler curves.

powers of  $(E'/E)$  and  $(1 - E'/E)$  in (8). But then again the contributions of these terms in (9) will mutually cancel each other to a large extent. In the expressions (9a) and (9b) even the term corresponding to  $a\rho^2$  occurring in (7) can be neglected entirely for the subsequent calculations. Since this term will give a term proportional to  $(E'/E)^2$  which again is multiplied by  $(\beta/E)^2 a/4$ , we shall be justified in retaining terms up to  $(E'/E)^2$  in  $\rho$  even if we neglect the term  $a\rho^2$  completely in (7). It will, however, be clear from fig 1 that for the region where these processes are of importance in the calculations of the Cascade Theory, the results obtained with the cross-sections given by (9) will be much more accurate than with the expressions for complete screening even in a heavier material as Pb. Moreover, the terms containing  $\rho^2, \rho^4, \dots$  in (7) will introduce terms containing  $(\beta/E)^2, (\beta/E)^4, \dots$

in (9a) and (9b). But it will appear from the method of obtaining  $P(E, t)$  and  $Q(E, t)$ , i.e. the number of particles and quanta in the energy range  $E$  and  $E+dE$ , that such terms will give a negligible contribution in comparison with that contributed by the term independent of  $\beta$  and also that containing  $(\beta/E)$ . Consequently, to the order of approximation we require in the present paper we can consider the expressions for the cross-sections given by (9), even without the last term, as fairly accurate. This we shall use in the subsequent calculations.

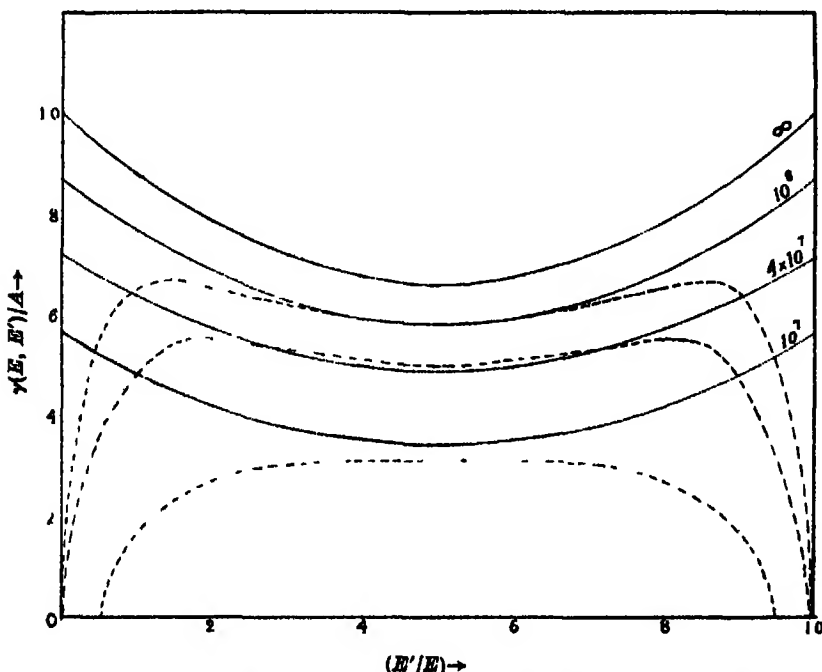


FIG 1(b). Differential probability of pair production per radiation length of Pb for quanta of various energies. Solid lines are those given by equation (9b). Dotted lines correspond to the Bethe-Heitler curves.

In addition to the process of pair creation considered above, quanta also suffer scattering by the Compton effect and at low energies this process is more frequent than pair creation. But in the energy range, with which we are concerned in the Cascade Theory, the energy loss due to Compton effect is very small, and so was neglected entirely in the previous papers. But in the present paper we can also take into account the effect of Compton scattering. The effective differential cross-section as deduced from the Klein-Nishina formula is

$$d\phi = \frac{1}{2} r_0^2 d\Omega \frac{k^2}{k_0^2} \left( \frac{k_0}{k} + \frac{k}{k_0} - \sin^2\theta \right) \quad \dots \quad (10)$$

where  $k_0, k$  are the initial and final energy of the quanta. Consequently, the average energy lost by a quantum per cm. path in a substance with atomic number  $Z$  is given by

$$NZ \int (k_0 - k) d\phi = \frac{1}{2} NZ k_0 r_0^2 \int \left( 1 - \frac{k}{k_0} \right) \left( \frac{k}{k_0} + \frac{k^2}{k_0^2} - \frac{k^2}{k_0^2} \sin^2\theta \right) \sin\theta d\theta d\omega \quad (11)$$

where  $k = k_0 [1 + \gamma(1 - \cos\theta)]^{-1}$  and  $\gamma = k_0/\mu$ ;  $\mu = mc^2$  .. .. (12)

Therefore if  $E$  be the energy of a light quantum, then due to Compton scattering the energy loss per cm of the path is given by (10), (11), and (12) by a simple integration so that

$$\left(-\frac{dE}{dx}\right)_{\text{comp}} = N Z \pi \mu r_0^2 \left[ \frac{2}{\gamma} + \left(1 - \frac{2}{\gamma} - \frac{3}{\gamma^2}\right) \log(1+2\gamma) - \left(1 - \frac{4}{\gamma} - \frac{3}{\gamma^2}\right) \frac{2\gamma}{1+2\gamma} + \frac{1}{2} \left(1 - \frac{2}{\gamma} - \frac{1}{\gamma^2}\right) \frac{2\gamma(2\gamma+2)}{(1+2\gamma)^2} - \frac{1}{3} \frac{2\gamma(4\gamma^2+4\gamma+3)}{(1+2\gamma)^3} \right] \quad \dots \quad (13)$$

For the range of energy with which we are concerned  $\gamma \gg 1$ , so that (13) reduces to

$$\left(-\frac{dE}{dx}\right)_{\text{comp}} \approx N Z \pi \mu r_0^2 \{ \log(1+2\gamma) - 5/6 \} \quad \dots \quad (13a)$$

Consequently, expressing lengths in the characteristic unit we get

$$\left(-\frac{dE}{dt}\right)_{\text{comp}} = \frac{137mc^2}{4Z} \frac{\pi}{\log(183Z^{-1/2})} [\log(1+2\gamma) - 5/6] = \beta' \text{ (say)} \quad (14)$$

Where  $\beta'$  can be treated as a constant, like the mean collision loss  $\beta$  for all energies. Moreover, as has already been stated in A it is now clear from (14) that  $\beta'$  will be between one-eighth and one-tenth of  $\beta$ . So that the error introduced due to the neglect of  $\beta'$  in the previous papers is negligible.

Following the general methods of the previous papers we see that the equations for  $P(E, t)$  and  $Q(E, t)$  are given by,

$$\begin{aligned} \frac{dP(E, t)}{dt} &= \int_0^\infty P(u, t) \pi(u, u-E) du - \int_0^E P(E, t) \pi(E, E-u) du \\ &\quad + 2 \int_E^\infty Q(u, t) \gamma(u, E) du + \beta \frac{\partial P(E, t)}{\partial E} \quad \dots \quad (15a) \end{aligned}$$

$$\frac{dQ(E, t)}{dt} = \int_E^\infty P(u, t) \pi(u, E) du - \int_0^E Q(E, t) \gamma(E, u) du + \beta' \frac{\partial Q(E, t)}{\partial E} \quad \dots \quad (15b)$$

where the last term on the right of (15b) represents the effect of Compton scattering.

As before, applying Mellin's transform and defining  $p(s, t)$ ,  $q(s, t)$  by the relations

$$p(s, t) = \int_0^\infty E^{s-1} P(E, t) dE; \quad q(s, t) = \int_0^\infty E^{s-1} Q(E, t) dE \quad \dots \quad (16)$$

we have after simplifications

$$\frac{dp(s, t)}{dt} = -A_s p(s, t) + B_s q(s, t) - \beta [ \{s-1-xa_s\} p(s-1, t) + xa_s q(s-1, t) ] \quad \dots \quad (17a)$$

$$\frac{dq(s, t)}{dt} = C_s p(s, t) - D_s q(s, t) - \beta [ xc_s p(s-1, t) + \{ (s-1)\beta'/\beta - xd \} q(s-1, t) ] \quad \dots \quad (17b)$$

where  $x = Z/82$  and  $A_s, B_s, C_s, D_s$  are functions of  $s$  and have been defined in A and B and

$$a_s = \left( \frac{7}{24} + \frac{1}{3} \alpha' \right) - \frac{1}{s} + \frac{5-2\alpha'}{2} \cdot \frac{1}{s+1} - \left( 2 - \frac{1}{2} \alpha' \right) \frac{1}{s+2} + \frac{1}{2} \frac{1}{s+3} \quad \dots \quad (18a)$$

$$b_s = 2 \left[ \frac{2}{s} - (2\alpha' + 1) \frac{1}{s+1} + (3\alpha' + 1) \frac{1}{s+2} - 2\alpha' \frac{1}{s+3} + \frac{\alpha'}{s+4} \right] \quad \dots \quad (18b)$$

$$c_s = \frac{1}{2} \left[ \frac{\alpha'}{s} - \frac{\alpha'-1}{s+2} + \frac{1}{s+3} \right] \quad \dots \quad (18c)$$

$$d = \left( \frac{11}{6} - \frac{3}{10} \alpha' \right) \quad \dots \quad (18d)$$

where

$$\alpha' = \left( \frac{4}{3} + \alpha \right)$$

It will be clear that the terms containing  $x$  in equations (17) are the correction terms introduced due to the modified forms of the cross-sections assumed, and when  $x$  is put equal to zero, they reduce to the equations given in A

Eliminating  $q(s, t)$  we have from (17)

$$\begin{aligned} \frac{d^2 p(s, t)}{dt^2} + (A_s + D) \frac{dp(s, t)}{dt} + (A_s D - B_s C_s) p(s, t) \\ = -\beta \left[ L_{s-1} p(s-1, t) + M_{s-1} \frac{dp(s-1, t)}{dt} \right] + O(\beta^2) + \end{aligned} \quad (19)$$

where

$$L_s = \{ D + \beta' A_s B_{s+1} / \beta B_s \} s - x \{ a_{s+1} D - B_{s+1} c_{s+1} - b_{s+1} c'_s + A_s d B_{s+1} / B_s \} \quad (20a)$$

$$M_s = \{ 1 + \beta' B_{s+1} / \beta B_s \} s - x \{ a_{s+1} + B_{s+1} d / B_s \} \quad (20b)$$

The boundary conditions are, as before, given by

$$p(s, 0) = E_0^{s-1}, \quad q(s, 0) = 0 \quad (21a)$$

for a shower excited by a particle of energy  $E_0$

So that from (17a) we have

$$\begin{aligned} \left\{ \frac{\partial}{\partial t} p(s, t) \right\}_{t=0} &= -A_s E_0^{s-1} - \beta \{ (s-1) - x a_s \} E_0^{s-2} \\ &= -E_0^{s-1} \left[ A_s + \frac{\beta}{E_0} \{ (s-1) - x a_s \} \right] \end{aligned} \quad (21b)$$

We obtain a solution of (19) subject to the boundary conditions given by (21a) and (21b)

As in A here also we assume for the solution of (19),

$$P(E, t) = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{ \frac{E_0}{E + \beta g^*(s, t)} \right\}^s f(s, t, \beta) ds \quad (22)$$

The assumptions as to the nature of the functions  $g^*(s, t)$  and  $f(s, t, \beta)$  are exactly the same as in the previous case. Consequently, following the general methods of the previous paper (A) it is easy to show that the boundary conditions for  $f(s, t, \beta)$  and  $g^*(s, t)$  for a particle-excited shower are given by

$$f(s, 0, \beta) = 1, \quad \left\{ \frac{\partial}{\partial t} f(s, t, \beta) \right\}_{t=0} = -A_s \quad \dots \quad (23)$$

and

$$g^*(s, 0) = 0; \quad \left\{ \frac{\partial}{\partial t} g^*(s, t) \right\}_{t=0} = 1 - x \frac{a_{s+1}}{s} \quad (24)$$

So that if we assume as before,

$$f(s, t, \beta) = f_0(s, t) + \left( \frac{\beta}{E_0} \right) f_1(s, t) + \left( \frac{\beta}{E_0} \right)^2 f_2(s, t) + \left( \frac{\beta}{E_0} \right)^3 f_3(s, t) + \dots \quad (25)$$

and substitute in (22), and insert the corresponding  $p(s, t)$  derived by (16) in (19), then it can be shown exactly as in A that

$$f_0(s, t) = \frac{D - \lambda_s}{\mu_s - \lambda_s} e^{-\lambda_s t} + \frac{\mu_s - D}{\mu_s - \lambda_s} e^{-\mu_s t} \quad (26)$$

where  $\lambda_s, \mu_s$  have the same values as in the previous case, and

$$(s-1)g^*(s-1, t)f_0(s-1, t) = h_s e^{-\lambda_s t} + j_s e^{-\mu_s t} \\ + \frac{L_{s-1} - M_{s-1}\lambda_{s-1}}{(\lambda_{s-1} - \lambda_s)(\lambda_{s-1} - \mu_s)} \frac{D - \lambda_{s-1}}{\mu_{s-1} - \lambda_{s-1}} e^{-\lambda_{s-1} t} + \frac{L_{s-1} - M_{s-1}\mu_{s-1}}{(\mu_{s-1} - \lambda_s)(\mu_{s-1} - \mu_s)} \frac{(\mu_{s-1} - D)e^{-\mu_{s-1} t}}{(\mu_{s-1} - \lambda_{s-1})},$$

where  $h_s, j_s$  are arbitrary functions of  $s$  independent of  $t$  and are to be determined so as to satisfy the boundary conditions (24)

We, thus, have

$$g^*(s, t) = \frac{1}{s} \left[ \frac{(L_s - M_s \lambda_s)(D - \lambda_s) \exp(-\lambda_s t)}{(\mu_s - \lambda_s)(\lambda_{s+1} - \lambda_s)(\mu_{s+1} - \lambda_s)} - \frac{(L_s - M_s \lambda_{s+1})(D - \lambda_{s+1}) \exp(-\lambda_{s+1} t)}{(\mu_{s+1} - \lambda_{s+1})(\lambda_{s+1} - \lambda_s)(\mu_s - \lambda_{s+1})} \right. \\ \left. + \frac{B_{s+1}}{B_s} \frac{x d - \beta' s / \beta}{\mu_{s+1} - \lambda_{s+1}} (e^{-\lambda_{s+1} t} - e^{-\mu_{s+1} t}) \right. \\ \left. + \frac{(L_s - M_s \mu_s)(D - \mu_s) \exp(-\mu_s t)}{(\mu_s - \lambda_s)(\mu_s - \lambda_{s+1})(\mu_{s+1} - \lambda_s)} - \frac{(L_s - M_s \mu_{s+1})(D - \mu_{s+1}) \exp(-\mu_{s+1} t)}{(\mu_{s+1} - \lambda_{s+1})(\mu_{s+1} - \lambda_s)(\mu_{s+1} - \mu_s)} \right] \\ \times \left[ \frac{D - \lambda_s}{\mu_s - \lambda_s} \exp(-\lambda_s t) + \frac{\mu_s - D}{\mu_s - \lambda_s} \exp(-\mu_s t) \right]^{-1} \quad (27)$$

So that, except for small  $t$  (when all the terms except the first term in both the numerator and denominator on the right side of (27) are negligible), we have

$$g^*(s, t) \approx \frac{1}{s} \left[ \frac{L_s - M_s \lambda_s}{(\lambda_{s+1} - \lambda_s)(\mu_{s+1} - \lambda_s)} \right] = \frac{L_s - M_s \lambda_s}{(D - \lambda_s)s} g_0(s) \\ \approx g_0^*(s) \quad (\text{say}). \quad \dots \quad (28)$$

The coefficient of  $g_0(s)$  on the right side of (28) reduces to 1 when  $x = 0$ , which it must be in order to satisfy the physical nature of the problem

It can be shown as in A that asymptotically for large  $s$

$$g^*(s, t) \approx t; \text{ for } \alpha' t < 1$$

$$g^*(s, t) \approx t + x \frac{\{D + \alpha'(1 - \gamma) - \frac{1}{2}\} d}{\alpha'^2} \frac{s^{\alpha' t}}{s(\log s)^2} \exp\{\alpha'(\gamma - 1) + \frac{1}{2} - D\} t; \text{ for } 1 < \alpha' t < 2,$$

and

$$g^*(s, t) \approx \frac{2}{\alpha' \log s} + x \frac{\{D + \alpha'(1 - \gamma) - \frac{1}{2}\} d}{2} s; \text{ for } \alpha' t > 2,$$

which shows at once that  $g^*(s, t) = g(s, t)$  when  $x = 0$ , even asymptotically. It may be noted here that for the convergence of the solution given by (22) it is only necessary that the real part of  $g^*(s, t)$  is not negative at any point of the contour for the  $s$ -integration. This has been shown by Iyengar (1942) and also by me in another paper. The condition that  $|g^*(s, t)| \rightarrow 0$ , when  $s \rightarrow \infty$  which was imposed in A is only a sufficient condition and is not necessary

From the tables given in A for the values of  $\lambda_s, \mu_s$ , etc. the values of  $L_s, M_s$  for different values of  $s$  can be easily obtained. The values of  $g^*(s, t)$  can then be derived with the help of (28)

The values of  $g^*(s, t)$  for any material can now be obtained by substituting proper values of  $x$ . For the purpose of comparing the results of the present paper with that of the previous papers we have also neglected the effect of the Compton scattering in the subsequent calculations, but, if necessary, this can also be retained in the general scheme. As discussed before, it is clear that the effect of the Compton scattering is very small compared to that of the other processes considered here.

The function  $f_1(s, t)$  is zero when  $g^*(s, t)$  is given by (27). The functions  $f_2(s, t)$ ,  $f_3(s, t)$ , can be calculated at once, but it can be shown, as in the previous papers, that the contribution of  $f_2(s, t)$  to the value of  $P(E, t)$  is usually small compared with that of  $f_0(s, t)$ . The contributions of the succeeding terms will be still smaller. It is, therefore, clear that an exact formal solution of (19) can be written in the form (22) with the functions  $f(s, t, \beta)$  and  $g^*(s, t)$  defined by (25), (26) and (27).

We thus have

$$P(E, t) = P_0(E, t) + P_2(E, t) + P_3(E, t) + \dots \quad (29)$$

where

$$P_0(E, t) = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{ \frac{E_0}{E + \beta g^*(s, t)} \right\}^s f_0(s, t) ds \quad (30)$$

$$P_2(E, t) = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left( \frac{\beta}{E_0} \right)^2 \left\{ \frac{E_0}{E + \beta g^*(s, t)} \right\}^s f_2(s, t) ds \quad (31)$$

and so on. It is now clear that a modification of the expressions for the cross-sections of the different processes, which was made in order to see the dependence of the cascades on the nature of the material, modifies the expression for the function  $g(s, t)$  defined in the previous papers, and has to be replaced by the function  $g^*(s, t)$  in the present case. The functions  $f_2(s, t)$ ,  $f_3(s, t)$  etc. will also be changed, but the consequent change in the final result due to them is insignificant.

Except for very small  $t$  the main contribution to (30) comes from the first term of  $f_0(s, t)$  containing  $\exp(-\lambda_s t)$  so that we can take

$$P_0(E, t) \approx \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{ \frac{E_0}{E + \beta g^*(s, t)} \right\}^s \frac{D - \lambda_s}{\mu_s - \lambda_s} e^{-\lambda_s t} ds. \quad (32)$$

The values of  $P_0(E, t)$  can now be calculated for different values of  $E$  and  $t$  by the saddle point method, and the methods of calculation have been shown in a previous paper (Chakrabarty, 1942).

To get the total number of particles  $N(E, t)$  whose energy is greater than  $E$ , one must integrate (22) with respect to  $E$  from  $E$  to  $\infty$ . We therefore have

$$N(E, t) = N_0(E, t) + N_2(E, t) + N_3(E, t) + \dots \quad (33)$$

where

$$N_0(E, t) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \left( \frac{E_0}{E + \beta g^*(s, t)} \right)^{s-1} \frac{1}{s-1} f_0(s, t) ds \quad (33a)$$

As discussed in A and B we can consider an electron, whose energy has fallen as low as twice the rest energy, i.e. about one million electron volts, as stopped. So that no electrons of lower energy need be considered in our calculations. The total number of particles in a shower is, therefore, given by

$$N(t) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{ \frac{E_0}{2mc^2 + \beta g^*(s, t)} \right\}^{s-1} \frac{1}{s-1} f(s, t, \beta) ds$$

$$= N_0(t) + N_2(t) + N_3(t) + \dots \quad (34)$$

where,

$$N_0(t) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{ \frac{E_0}{2mc^2 + \beta g^*(s, t)} \right\}^{s-1} \frac{1}{s-1} f_0(s, t) ds \quad (34a)$$

As in B here also we can neglect the term  $2mc^2$  in (34) except for very small  $t$

Equations (33a) and (34a) give respectively the first terms of a series, of which the successive terms come through  $P_2(E, t)$ ,  $P_3(E, t)$  in (29), but the contribution of these terms is much smaller than that due to  $P_0(E, t)$ . Consequently, (33a) and (34a) can be considered as giving the values of  $N(E, t)$  and  $N(t)$  respectively with an error which can be shown as in B to be less than 30 p.c. except for thicknesses so great that the shower has been completely absorbed. In the position of the maximum, the error is certainly less than 10 p.c. But in any case, the values of  $P_0(E, t)$ ,  $N_0(E, t)$  and  $N_0(t)$  obtained in the present paper when compared with the corresponding values obtained in A and B will show quite accurately the effect of screening on the pair-creation and radiation cross-sections and also its consequence on the Cascade Theory

For a given value of  $E_0$  the maximum of  $N_0(t)$  except for very small  $t$  occurs\* at such a value of  $t$  that the corresponding value of  $s_0$  is 2, i.e. when  $\lambda_s = 0$ . Calling this value  $t_m$  it follows that

$$t_m = \frac{1}{\lambda_s^2} \left[ y_0 + \frac{d}{ds} \left\{ \log \left( \frac{D-\lambda_s}{\mu_s-\lambda_s} \frac{1}{s-1} \right) - (s-1) \log (2mc^2/\beta + g_0^*(s)) \right\} \right]_{s=2} \quad (35a)$$

and the corresponding value of  $N_m$  is given by

$$N_m = \frac{\exp y_0}{\sqrt{2\pi\psi^{**}(2)} \mu_s} \frac{D}{\mu_s} \left\{ 2mc^2/\beta + g_0^*(2) \right\}^{-1},$$

where

$$\psi^*(s) = (s-1)y_0 - \lambda_s t + \log \left[ \frac{D-\lambda_s}{\mu_s-\lambda_s} \frac{1}{s-1} \left( \frac{2mc^2}{\beta} + g_0^*(s) \right)^{-(s-1)} \right],$$

and

$$y_0 = \log_s(E_0/\beta)$$

From (27) and (28) it is clear that except for very small  $t$ ,  $g^*(s, t) \approx g_0^*(s)$  so that with this approximation (a similar approximation was also made in B) we get for Pb and air,

$$t_m(\text{Pb}) = 1.01 y_0 - 0.920 \quad (36a)$$

$$t_m(\text{air}) = 1.01 y_0 - 1.856 \quad (36b)$$

and consequently,

$$N_m(\text{Pb}) = 0.628 \frac{\exp y_0}{\{2\pi(1.561t_m + 2.203)\}^{\frac{1}{2}}} = 0.199 (y_0 + 0.486)^{-\frac{1}{2}} \exp y_0 \quad (37a)$$

$$N_m(\text{air}) = 0.537 \frac{\exp y_0}{\{2\pi(1.561t_m + 0.124)\}^{\frac{1}{2}}} = 0.171 (y_0 - 1.76)^{-\frac{1}{2}} \exp y_0 \quad (37b)$$

Equation (36) shows that for a given value of  $y_0$  the maximum of  $N_0(t)$  occurs at a greater thickness for heavier material, the value of  $N_m$ , however, depends on the value of  $y_0$ . The values of  $N(t)$  can now be calculated for different values of  $y_0$  and  $t$  and also for different materials by taking the corresponding values of  $r$ . In Table II the values of  $N_0(t)$  for showers produced in Pb have been given for different values of  $y_0$  and only for two different values of  $t$ , viz. 4 and 10. The corresponding values obtained in B have also been included for comparison. For  $t = 10$ , the values of  $N_0(t)$  for air have also been given. The table shows the dependence of the Cascades on the nature of the material

\* Cf footnote on page 473 in B.

TABLE II.

Values of  $N_0(t)$  for different values of  $y_0$  and  $t$  in Pb and air.  $N_0^B(t)$  represents the corresponding values as obtained in B

$y_0 \backslash t$		3	5	7	9	12	16
4	$N_0^{Pb}(t)$	1 390	12 47	60 40	206 2	932 9	4570
	$N_0^B(t)$	1 181	13 78	69 91	241 2	1117	5439
10	$N_0^{Pb}(t)$	0 1601	3 215	45 97	466 3	8682	195300
	$N_0^{air}(t)$	0 0440	1 749	33 51	405 6	8357	226700
	$N_0^B(t)$	0 0366	1 613	33 26	392 2	8073	229500

Corben (1941) has given an analysis for the calculations of Cascades in a heavy material, where he has taken Serber's results as the basis of his calculations. For reasons already mentioned in A and also in another paper (Chakrabarty, 1942) these results are seriously open to doubts. Corben's expression for  $N(t)$  is a series in ascending powers of  $t$  and it is very difficult to estimate how far it is possible to use his result for large  $t$ . In fact, for large values of  $t$  the expansion has little meaning as the author himself realises. Moreover, he has ultimately neglected the variation in the cross-section for the Bremsstrahlung process. There is, however, one important difference between the present analysis and that of Corben. Whereas the present analysis reveals that the modification of the cross-sections shifts the position of the maximum of the shower transition curve to a greater depth, Corben has stated that the corresponding shift is in the opposite direction. The values of  $N_m$  for a given  $E_0$ , as given by Corben are much higher than that obtained here, which is probably due mainly to a similar discrepancy between the values of  $N_m$  given by Serber and that obtained in B. In Table III the values of  $N_m$  for some given values of

TABLE III.

$E_0/\beta$	155	1550	15500
$N_m(Pb)$	13 2 (13.5)	110 (148)	971 (1550)
$t_m(Pb)$	4 17	6 49	8.82
$N_m(air)$	14 6 (21.9)	112 (200)	944 (1940)
$t_m(air)$	3 23	5 55	7.88
$\frac{N_m(S)}{N_m(B)}$	1.53	1 65	1 71

$E_0/\beta$ , have been given for two different materials, viz, Pb and air, together with those obtained by Corben, which are placed within brackets. In the last row of the table is given the ratio of the values of  $N_m$  as obtained by Serber to that obtained in B. The values of  $t_m$  for Pb and air as obtained from the present analysis are also included in the table.

Since the modified forms of the cross-sections, as compared to the original ones considered in A, show a greater probability of emitting relatively low energy quanta and these low energy quanta in turn will have a lower probability of creating pairs, it is clear that at the beginning the number of shower particles will be less. Also, since the mean radiation loss is now less, the shower production process will continue to a greater thickness of the material. Due to the reduction of both the radiation and pair creation cross-sections the whole curve is shifted in heavy materials towards greater depths. In effect the characteristic length is slightly increased\*. The change in the pair-creation cross-sections, however, will give a greater number of particles as compared to the previous one, beyond the maximum of the transition curve. Whereas this later variation has also been obtained by Corben, the former ones are just opposite to what Corben has obtained. All the above mentioned features are clearly shown in fig. 2, where the shower transition curves for a given  $y_0$  (say  $y_0 = 6$ ) have been drawn both for Pb and air, together with the similar curve obtained when the variation of the cross-sections are neglected as was done in the previous papers (A and B).

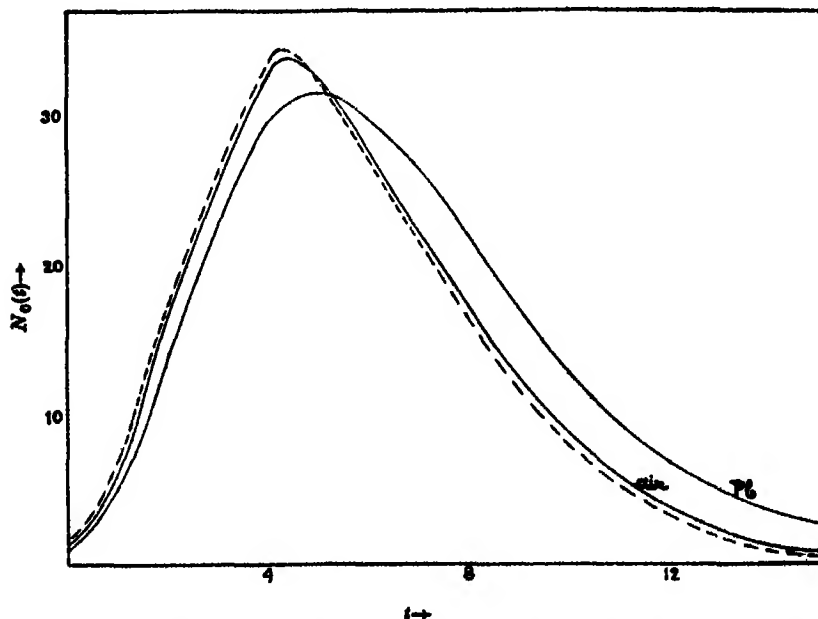


FIG. 2 Shower transition curves in Pb and air for a primary particle of energy  $\beta e^0$ . Dotted curve corresponds to the case of complete screening

In the previous paper (A) we have shown purely on the basis of physical considerations that the inaccuracies introduced due to the approximations made on the expressions for the cross-sections will be much less than 20 p.c. in the case of air but will be of the order of 20 p.c. in the case of Pb. We can see now from fig. 2, how far this is true.

\* I am indebted to Dr. Bhabha for pointing out this to me in a private communication.

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# POLARISATION OF THE VACUUM IN THE MESON THEORY

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## ABSTRACT

Expressions, correct to the first order in  $e^2$ , are obtained for the charges induced in the vacuum of the vector and scalar meson theories by an electric field which is assumed to be much smaller than a critical field. The method of calculation that has been followed is somewhat similar to the subtraction formalism of the positron theory. The deviations due to the existence of the polarisation of the vacuum from Coulomb's law for the mutual potential energy of point charges have been calculated. The effect of these deviations in modifying the Coulomb scattering law for heavy particles has also been discussed.

## INTRODUCTION

It has been shown by various authors (Dirac, 1934, Heisenberg, 1934, Furry and Oppenheimer, 1934, Pierls, 1934, Serber, 1935, Uehling, 1935, Weisskopf, 1936) that the theory of positron produces certain modifications in the Maxwell field equations by the addition of terms which may be linear and non-linear. These modifications occur as the electromagnetic field induces a charge and current distributions due to the creation and annihilation of electron-positron pairs. The presence of the non-linear terms invalidates the principle of superposition of two fields, and gives rise to some processes which are impossible in principle according to ordinary electrodynamics, viz the process of scattering of light by light, etc. The linear terms, on the other hand, give a non-vanishing polarisability of the vacuum.

The vacuum of the meson theory has also analogous properties. In this theory the existence of positively and negatively charged particles, and the creation and annihilation of meson pairs are the natural consequences of the theory without any special assumption about the vacuum as in the positron theory. But the general problem here is much more complicated than that in the positron theory. In this note, for the sake of simplicity, we wish to investigate the effect which modifies the Maxwell field equations by the addition of linear terms, that is, which corresponds to a non-vanishing polarisability of the vacuum in the meson theory. Furthermore we shall restrict ourselves to the case which is produced by a rapidly varying external electric field. For this purpose we shall start with the Duffin-Kemmer's (1939) formulation of the meson theory, the advantage of this formulation is that the results for theories of particles with spin one and zero are obtained from a single scheme.

As in the positron theory we shall assume that the critical field strength of the meson theory is  $F_c = \frac{m^2 c^3}{\hbar e}$  and restrict ourselves in those regions of space in which the external field intensity is small compared to the critical field, but with no restrictions on the variation of this intensity. Further this field is to be considered switched on adiabatically increasing from zero to some constant value corresponding to the presence of the external charges. On these assumptions an expression for the induced charge distribution will be deduced, defining this quantity as the difference between the contributions to the expectation value of the vacuum distribution in the presence and absence of an external electric field. This expression, however, does not turn out to be finite and cannot give any sensible interpretation to the problem. A quite similar situation also arose in the positron theory, where Heisenberg following the suggestion of Dirac

was able to obtain unconditionally convergent expressions for the expectation values of the physical quantities, this convergence is achieved by taking the density matrix in non-diagonal form and subtraction from it of all the singular terms. It is of course possible also to subtract finite terms. Heisenberg has included such a term and his definition of the physical quantities is, of course, consistent with the vanishing of the polarisation of the vacuum for slowly varying and weak fields. In this paper following the method of Pauli and Rose (1936) a similar subtraction formalism will also be adopted to ignore the singular terms in the induced charged distribution and to obtain finite deviation which can be given an unambiguous meaning. We shall not discuss here the question of uniqueness of the result, nor we shall claim it.

## 1 EQUATIONS OF MESON AND PERTURBATION THEORY

The meson is defined in the presence of the electromagnetic field by the wave equation

$$\left(\frac{\partial}{\partial x_\mu} - \frac{ie}{\hbar c} A_\mu\right) \beta_\mu \psi + \kappa \psi = 0 \quad (1)$$

where  $\kappa = \frac{mc}{\hbar}$ ,  $x_4 = ict$ . The  $\beta$ -operators satisfy the commutation rules

$$\beta_\mu \beta_\nu \beta_\rho + \beta_\rho \beta_\nu \beta_\mu = \beta_\mu \delta_{\nu\rho} + \beta_\rho \delta_{\nu\mu} \quad \dots \quad (2)$$

The equation of supplementary condition is given by

$$\left(\frac{\partial}{\partial x_k} - \frac{ie}{\hbar c} A_k\right) \beta_k \beta_4^2 \psi + \kappa (1 - \beta_4^2) \psi = 0 \quad \dots \quad (3)$$

with the help of which we can eliminate those components of  $\psi$  for which  $\beta_4 \psi$  is zero and which are not directly quantised. Repeated suffixes mean summation, Greek suffixes run from 1 to 4 and Latin from 1 to 3.

The plane wave solution of the equation of free meson is

$$\phi_m = \frac{1}{\sqrt{V}} u_m \exp \{ -ie_m E_m t / \hbar + i(\mathbf{p}_m \mathbf{r}) / \hbar \} \quad \dots \quad (4)$$

where  $\varepsilon_m = \pm 1$ ,  $E_m = c(p_m^2 + m^2 c^2)^{\frac{1}{2}}$ . In the vector meson theory (spin one), the  $\beta$ 's are ten-row square matrices and  $u$ 's are column matrices of ten elements. For a given  $\mathbf{p}$  there are six linearly independent solutions of the form (4), three of which are associated with the positively charged states for which  $\varepsilon_m = +1$  and three with the negatively charged states for which  $\varepsilon_m = -1$ , and correspond to the three states of polarisation which are taken to be transverse and longitudinal to the direction of motion. In the scalar meson theory (spin zero), the  $\beta$ 's are five-row square matrices, there are two linearly independent solutions, one of which is associated with the positively charged state and the other with the negative one, and the polarisation is longitudinal.

We suppose that the meson to be initially in the state  $\phi_n$ . At any subsequent time after the introduction of the field let the wave function be  $\psi_n$  which is expanded as

$$\psi_n = \sum_m c_{nm} \phi_m \quad \dots \quad (5)$$

We now write the equation (1) in the form

$$\left(\beta_\mu \frac{\partial}{\partial x_\mu} + \kappa\right) \psi = \frac{ie}{\hbar c} A_\mu \beta_\mu \psi,$$

and eliminate with the help of (3) from the right hand side those components of  $\psi$  for which  $\beta_4\psi$  is zero, and get

$$\left(\beta_\mu \frac{\partial}{\partial x_\mu} + \kappa\right)\psi = \frac{ie}{\hbar c} A_\mu \beta_\mu \left\{1 - \frac{1}{\kappa} \beta_k \frac{\partial}{\partial x_k}\right\} \beta_4^2 \psi - \frac{e^2}{\hbar^2 c^2 \epsilon_\kappa} (\mathbf{A}\beta)^2 \beta_4^2 \psi \quad (6)$$

Now since

$$\left(\beta_\mu \frac{\partial}{\partial x_\mu} + \kappa\right)\phi_m = 0, \text{ and } \beta_k \beta_4^2 \frac{\partial \phi_m}{\partial x_k} + \kappa(1 - \beta_4^2)\phi_m = 0$$

we have from (5) and (6)

$$\frac{1}{ic} \sum_m c_{nm} \beta_4 \phi_m = \frac{ie}{\hbar c} \sum_m c_{nm} \left\{ A_\mu \beta_\mu + \frac{ie}{\hbar c \kappa} (\mathbf{A}\beta)^2 \beta_4^2 \right\} \phi_m \quad (7)$$

Multiplying by  $\phi_r^\dagger$  on the left and integrating over the whole co-ordinates space and applying the normalising condition

$$\frac{1}{i} \int \phi_r^\dagger \beta_4 \phi_m d\mathbf{r} = \epsilon_r \delta_{rm}$$

where  $\phi_r^\dagger = i\phi_r^* \eta_4$ ,  $\eta_4 = 2\beta_4^2 - 1$ , we obtain

$$c_{nr}(t) = \frac{ie}{\hbar} \sum_m c_{nm} H_{mr} \exp \frac{i}{\hbar} (\epsilon_r E_r - \epsilon_m E_m) t, \quad (8)$$

where

$$H_{mr} = \frac{e}{V} \int u_r^\dagger \left\{ A_\mu \beta_\mu + \frac{ie}{\hbar c \kappa} (\mathbf{A}\beta)^2 \beta_4^2 \right\} u_m \exp \frac{i}{\hbar} (\mathbf{p}_m - \mathbf{p}_r, \mathbf{r}) d\mathbf{r} \quad (9)$$

For the sake of simplicity we shall work out the case in which  $\mathbf{A} = 0$  and  $A_0 \neq 0$  and be interested only in the charge density but not in the current density. Since we shall confine ourselves to the approximation in which effects proportional to the powers of the constant  $\alpha = \frac{e^2}{\hbar c}$  higher than the first will be neglected, there will be no loss of generality if we expand  $A_0$  in plane waves of which the one Fourier component is

$$A_0 = a_0 \exp \frac{i}{\hbar} \{ (\mathbf{k}\mathbf{r}) - ck_0 t \} + \text{conj}, \text{ and } \mathbf{A} = 0, \quad (10)$$

where  $\mathbf{k}$  is the propagation vector, and according to the Maxwell equations

$$j_0(\mathbf{r}) = \frac{k^2}{4\pi\hbar^2} A_0(\mathbf{r}) \quad (11)$$

where  $j_0(\mathbf{r})$  is the charge density which produces the field  $A_0$

Then following the method and assumption of Heisenberg (1934), we get in the usual way from (8), (9) and (10)

$$c_{nm}(t) = -e\epsilon_m \left[ u_n(\mathbf{p}_n + \mathbf{k})^* \beta_4 u(\mathbf{p}_n) - \frac{a_0 \exp \frac{i}{\hbar} (\epsilon_m E_m - \epsilon_n E_n - ck_0 t)}{\epsilon_m E_m - \epsilon_n E_n - ck_0} \right. \\ \left. + u_n(\mathbf{p}_n - \mathbf{k})^* \beta_4 u(\mathbf{p}_n) - \frac{a_0^* \exp \frac{i}{\hbar} (\epsilon_m E_m - \epsilon_n E_n + ck_0 t)}{\epsilon_m E_m - \epsilon_n E_n + ck_0} \right] + \delta_{nm}.$$

Hence the solution of the equation (1) in the first order perturbation theory when  $A_\mu$  is given by (10) can be written in the form

$$\psi^\pm(\mathbf{p}, \mathbf{r}) = \phi^\pm(\mathbf{p}, \mathbf{r}) + \phi^\pm(\mathbf{p}, \mathbf{r})' \quad \dots \quad (12)$$

where

$$\begin{aligned}
 \phi^{\pm}(\mathbf{p}, \mathbf{r})' = & -e \left[ u^{+}(\mathbf{p}+\mathbf{k})^{*} \beta_4 u^{\pm}(\mathbf{p}) \frac{a_0 \exp \frac{i}{\hbar} \{E(\mathbf{p}+\mathbf{k}) \mp E(\mathbf{p}) - ck_0\} t}{E(\mathbf{p}+\mathbf{k}) \mp E(\mathbf{p}) - ck_0} \phi^{+}(\mathbf{p}+\mathbf{k}, \mathbf{r}) \right. \\
 & + u^{-}(\mathbf{p}+\mathbf{k})^{*} \beta_4 u^{\pm}(\mathbf{p}) \frac{a_0 \exp. - \frac{i}{\hbar} \{E(\mathbf{p}+\mathbf{k}) \pm E(\mathbf{p}) + ck_0\} t}{E(\mathbf{p}+\mathbf{k}) \pm E(\mathbf{p}) + ck_0} \phi^{-}(\mathbf{p}+\mathbf{k}, \mathbf{r}) \\
 & + u^{+}(\mathbf{p}-\mathbf{k})^{*} \beta_4 u^{\pm}(\mathbf{p}) \frac{a_0^{*} \exp \frac{i}{\hbar} \{E(\mathbf{p}-\mathbf{k}) \mp E(\mathbf{p}) + ck_0\} t}{E(\mathbf{p}-\mathbf{k}) \mp E(\mathbf{p}) + ck_0} \phi^{+}(\mathbf{p}-\mathbf{k}, \mathbf{r}) \\
 & \left. + u^{-}(\mathbf{p}-\mathbf{k})^{*} \beta_4 u^{\pm}(\mathbf{p}) \frac{a_0^{*} \exp - \frac{i}{\hbar} \{E(\mathbf{p}-\mathbf{k}) \pm E(\mathbf{p}) - ck_0\} t}{E(\mathbf{p}-\mathbf{k}) \pm E(\mathbf{p}) - ck_0} \phi^{-}(\mathbf{p}-\mathbf{k}, \mathbf{r}) \right]. \quad (13)
 \end{aligned}$$

where the index + or - corresponds to positively or negatively charged state

## 2 THE INDUCED CHARGE DENSITY.

The charge density in the present theory is defined by

$$\rho = e\psi(\mathbf{r}')^{*} \beta_4 \psi(\mathbf{r}'')$$

Following Heisenberg's rule we replace this charge density as in a previous paper of the present author (1943) by

$$\rho = \frac{e}{2} \{ \psi(\mathbf{r}')^{*} \beta_4 \psi(\mathbf{r}'') + \beta_4 \psi(\mathbf{r}'') \psi(\mathbf{r}')^{*} \beta_4^2 \} \quad \dots \quad (14)$$

where in the second term  $\beta_4 \psi$  is a single row matrix and  $\psi^{*} \beta_4^2$  is a single column matrix, and this definition is taken for symmetrising the density matrix between positively and negatively charged mesons. Now if

$$\psi_0 = \sum_p \{ a(\mathbf{p}) \phi^{+}(\mathbf{p}) + b^{*}(\mathbf{p}) \phi^{-}(\mathbf{p}) \} \quad \dots \quad (15)$$

is the wave function unperturbed by the field and  $\psi_1$  is the correction in the first order perturbation theory, then

$$\psi_1 = \sum_p \{ a(\mathbf{p}) \phi^{+}(\mathbf{p})' + b^{*}(\mathbf{p}) \phi^{-}(\mathbf{p})' \} \quad \dots \quad (16)$$

where  $\phi^{+}(\mathbf{p})'$  and  $\phi^{-}(\mathbf{p})'$  are given by (13). Hence

$$\langle \mathbf{r}' | \rho | \mathbf{r}'' \rangle = \langle \mathbf{r}' | \rho_0 | \mathbf{r}'' \rangle + \langle \mathbf{r}' | \delta \rho | \mathbf{r}'' \rangle$$

where

$$\langle \mathbf{r}' | \rho_0 | \mathbf{r}'' \rangle = \frac{e}{2} \{ \psi_0(\mathbf{r}')^{*} \beta_4 \psi_0(\mathbf{r}'') + \beta_4 \psi_0(\mathbf{r}'') \cdot \psi_0(\mathbf{r}')^{*} \beta_4^2 \} \quad \dots \quad (17)$$

and

$$\begin{aligned}
 \langle \mathbf{r}' | \delta \rho | \mathbf{r}'' \rangle = & \frac{e}{2} \{ \psi_0(\mathbf{r}')^{*} \beta_4 \psi_1(\mathbf{r}'') + \beta_4 \psi_0(\mathbf{r}'') \psi_1(\mathbf{r}')^{*} \beta_4^2 \\
 & + \psi_1(\mathbf{r}')^{*} \beta_4 \psi_0(\mathbf{r}'') + \beta_4 \psi_1(\mathbf{r}'') \cdot \psi_0(\mathbf{r}')^{*} \beta_4^2 \} \quad \dots \quad (18)
 \end{aligned}$$

to a first approximation. If (15) and (16) are now substituted in (17) and (18) and only the diagonal elements with respect to time variable are retained,  $\langle \mathbf{r}' | \rho_0 | \mathbf{r}'' \rangle$  for the vacuum vanishes while (18) in non-diagonal form in space co-ordinates becomes

$$\langle \mathbf{r}' | \delta \rho | \mathbf{r}'' \rangle = \frac{e}{2} \sum_p [(2N^+(p)+1) \{ \phi^+(p, \mathbf{r}')^* \beta_4 \phi^+(p, \mathbf{r}'')' + \phi^+(p, \mathbf{r}')^* \beta_4 \phi^+(p, \mathbf{r}'') \} \\ + (2N^-(p)+1) \{ \phi^-(p, \mathbf{r}')^* \beta_4 \phi^-(p, \mathbf{r}'')' + \phi^-(p, \mathbf{r}')^* \beta_4 \phi^-(p, \mathbf{r}'') \}]$$

where  $N^+(p)$  and  $N^-(p)$  give the number of positive and negative mesons in the state  $p$ . For the vacuum  $N^+(p) = N^-(p) = 0$ , and we get

$$\langle \mathbf{r}' | \delta \rho | \mathbf{r}'' \rangle = \frac{e}{2} \sum_p [\phi^+(p, \mathbf{r}')^* \beta_4 \phi^+(p, \mathbf{r}'')' + \phi^+(p, \mathbf{r}')^* \beta_4 \phi^+(p, \mathbf{r}'') \\ + \phi^-(p, \mathbf{r}')^* \beta_4 \phi^-(p, \mathbf{r}'')' + \phi^-(p, \mathbf{r}')^* \beta_4 \phi^-(p, \mathbf{r}'')]$$

Then by (13) after some calculations this assumes the form

$$\langle \mathbf{r}' | \delta \rho | \mathbf{r}'' \rangle = -\frac{e^2}{V} \sum_q \left[ \frac{\{ u^-(q+\mathbf{k}/2)^* \beta_4 u^-(q-\mathbf{k}/2) \} \{ u^+(q-\mathbf{k}/2)^* \beta_4 u^-(q+\mathbf{k}/2) \}}{E(q+\mathbf{k}/2) + E(q-\mathbf{k}/2) + ck_0} \right. \\ \left. + \frac{\{ u^+(q+\mathbf{k}/2)^* \beta_4 u^-(q-\mathbf{k}/2) \} \{ u^-(q-\mathbf{k}/2)^* \beta_4 u^+(q+\mathbf{k}/2) \}}{E(q+\mathbf{k}/2) + E(q-\mathbf{k}/2) - ck_0} \right] A_0(\mathbf{R}) \exp \frac{i}{\hbar} (\mathbf{q}\mathbf{r}) \quad (19)$$

where

$$\mathbf{R} = \frac{\mathbf{r}' + \mathbf{r}''}{2}, \quad \mathbf{r} = \mathbf{r}'' - \mathbf{r}' \quad \dots \quad (20)$$

We shall now sum over the directions of polarisation in the states  $q+\mathbf{k}/2$  and  $q-\mathbf{k}/2$ , the detail method of which and of the subsequent spur calculations are given by Booth and Wilson (1940). On performing the above operations and replacing the summation over  $q$  by integration, (19) assumes the form\*

$$\langle \mathbf{r}' | \delta \rho^0 | \mathbf{r}'' \rangle = -\frac{e^2}{2c} \frac{A_0(\mathbf{R})}{(2\pi\hbar)^3} \int \frac{(\epsilon + \epsilon')(\epsilon - \epsilon')^2}{\epsilon\epsilon' \{ (\epsilon + \epsilon')^2 - k_0^2 \}} \exp \frac{i}{\hbar} (\mathbf{q}\mathbf{r}) d\mathbf{q} \quad (21a)$$

for the scalar meson theory (spin zero), and

$$\langle \mathbf{r}' | \delta \rho^1 | \mathbf{r}'' \rangle = -\frac{3e^2}{2c} \frac{A_0(\mathbf{R})}{(2\pi\hbar)^3} \int \frac{\epsilon + \epsilon'}{\epsilon\epsilon' \{ (\epsilon + \epsilon')^2 - k_0^2 \}} \{ (\epsilon - \epsilon')^2 \\ + \frac{2}{3m^2c^2} (q^2k^2 - (\mathbf{q}\mathbf{k})^2) \} \exp \frac{i}{\hbar} (\mathbf{q}\mathbf{r}) d\mathbf{q} \quad (21b)$$

for the vector meson theory (spin one), where

$$\epsilon = [(q-\mathbf{k}/2)^2 + m^2c^2]^{\frac{1}{2}}, \quad \epsilon' = [(q+\mathbf{k}/2)^2 + m^2c^2]^{\frac{1}{2}} \quad \dots \quad (22)$$

For  $k_0 = 0$  the expression (21a) for the scalar meson theory is in agreement with the corresponding expression given by Pauli and Weisskopf (1934). The expressions (21a) and (21b) are the differences between the charge density matrix in the presence and the absence of the external field in the approximation in question. They are the Fourier amplitudes

\* Throughout the paper the results with index 0 refer to the scalar meson theory and with index 1 to the vector meson theory.

of the charge induced by an electric field which is everywhere small compared to the critical field  $F_c = \frac{m^2 c^3}{\hbar e}$ . Using the relation (11), (21a) can be written in the form

$$\begin{aligned} \langle \mathbf{r}' | \delta \rho^0 | \mathbf{r}'' \rangle &= -\frac{\alpha}{8\pi^2} \frac{k^2}{\hbar^2} A_0(\mathbf{R}) F^0(\mathbf{k}, k_0, \mathbf{r}) \\ &= -\frac{\alpha}{2\pi} J_0(\mathbf{R}) F^0(\mathbf{k}, k_0, \mathbf{r}) \end{aligned} \quad (23a)$$

where

$$F^0(\mathbf{k}, k_0, \mathbf{r}) = \frac{1}{2\pi k^2} \int \frac{(\epsilon + \epsilon')(\epsilon - \epsilon')^2}{\epsilon \epsilon' \{(\epsilon + \epsilon')^2 - k_0^2\}} \exp \frac{i}{\hbar} (\mathbf{q}\mathbf{r}) d\mathbf{q}, \quad (24a)$$

and (21b) in the form

$$\begin{aligned} \langle \mathbf{r}' | \delta \rho^1 | \mathbf{r}'' \rangle &= -\frac{3\alpha}{8\pi^2} \frac{k^2}{\hbar^2} A_0(\mathbf{R}) F^1(\mathbf{k}, k_0, \mathbf{r}) \\ &= -\frac{3\alpha}{2\pi} J_0(\mathbf{R}) F^1(\mathbf{k}, k_0, \mathbf{r}) \end{aligned} \quad (23b)$$

where

$$F^1(\mathbf{k}, k_0, \mathbf{r}) = \frac{1}{2\pi k^2} \int \frac{(\epsilon + \epsilon')}{\epsilon \epsilon' \{(\epsilon + \epsilon')^2 - k_0^2\}} \left\{ (\epsilon - \epsilon')^2 + \frac{2}{3m^2 c^2} (q^2 k^2 - (\mathbf{q}\mathbf{k})^2) \right\} \exp \frac{i}{\hbar} (\mathbf{q}\mathbf{r}) d\mathbf{q} \quad (24b)$$

For  $\mathbf{r} = 0$  the integrals (24a) and (24b) do not turn out to be finite. Following the method in the positron theory we shall introduce suitably chosen subtractive terms depending on  $\mathbf{r}$  in such a way that the difference is finite for  $\mathbf{r} = 0$ . These subtractive terms will in general be the singular terms. It is of course possible also to subtract the finite terms. These terms are to be so chosen that they normalise the polarisation of the vacuum for slowly varying and weak fields to zero. For this purpose the method of Pauli and Rose is followed here. For large  $q$  or what turns out to be the same for small values of  $k$ ,

$$\epsilon \sim \epsilon' \sim (m^2 c^2 + q^2)^{\frac{1}{2}}$$

and to a better approximation

$$\begin{aligned} (\epsilon - \epsilon')^2 &\sim \frac{(\mathbf{q}\mathbf{k})^2}{(m^2 c^2 + q^2)}, \\ \left[ \epsilon \epsilon' (\epsilon + \epsilon') \left\{ 1 - \frac{k_0^2}{(\epsilon + \epsilon')^2} \right\} \right]^{-1} &\sim \frac{1}{2(m^2 c^2 + q^2)^{\frac{3}{2}}} \left\{ 1 - \frac{3}{8} \frac{k^2}{m^2 c^2 + q^2} \right. \\ &\quad \left. + \frac{5}{8} \frac{(\mathbf{q}\mathbf{k})^2}{(m^2 c^2 + q^2)^2} + \frac{1}{4} \frac{k_0^2}{m^2 c^2 + q^2} \right\} \end{aligned}$$

So we can split up each of the integrals (24a) and (24b) into two terms

$$F^0(\mathbf{k}, k_0, \mathbf{r}) = F_1^0(\mathbf{k}, k_0, \mathbf{r}) + F_2^0(\mathbf{k}, k_0, \mathbf{r}), \quad (25a)$$

and

$$F^1(\mathbf{k}, k_0, \mathbf{r}) = F_1^1(\mathbf{k}, k_0, \mathbf{r}) + F_2^1(\mathbf{k}, k_0, \mathbf{r}), \quad (25b)$$

where

$$F_1^0(\mathbf{k}, k_0, \mathbf{r}) = \frac{1}{4\pi} \int \left[ \frac{q^2 \cos^2 \theta}{m^2 c^2 + q^2} \right] \frac{\exp \frac{i}{\hbar} (\mathbf{q}\mathbf{r})}{(m^2 c^2 + q^2)^{\frac{1}{2}}} d\mathbf{q}, \quad (26a)$$

and

$$F_1^1(\mathbf{k}, k_0, \mathbf{r}) = \frac{1}{4\pi} \int \left[ \frac{q^2 \cos^2 \theta}{m^2 c^2 + q^2} + \frac{2q^2 \sin^2 \theta}{3m^2 c^2} \left\{ 1 - \frac{1}{8(m^2 c^2 + q^2)} (3k^2 - 5k^2 \cos^2 \theta - 2k_0^2) \right\} \right] \\ \times \frac{\exp \frac{i}{\hbar} (\mathbf{q}\mathbf{r})}{(m^2 c^2 + q^2)^{\frac{1}{2}}} d\mathbf{q}, \quad (26b)$$

$\theta$  being the angle between  $\mathbf{q}$  and  $\mathbf{k}$ , and where for  $r = 0$

$$f^0(\mathbf{k}, k_0) = F_2^0(\mathbf{k}, k_0, 0) = \frac{1}{2\pi k^2} \int \left[ \frac{(\epsilon + \epsilon')(\epsilon - \epsilon')^2}{\epsilon \epsilon' \{ (\epsilon + \epsilon')^2 - k_0^2 \}} - \frac{k^2}{2} \frac{q^2 \cos^2 \theta}{(m^2 c^2 + q^2)^{\frac{1}{2}}} \right] d\mathbf{q}, \quad (27a)$$

and

$$f^1(\mathbf{k}, k_0) = F_2^1(\mathbf{k}, k_0, 0) = \frac{1}{2\pi k^2} \int \left[ \frac{\epsilon + \epsilon'}{\epsilon \epsilon' \{ (\epsilon + \epsilon')^2 - k_0^2 \}} \left\{ (\epsilon - \epsilon')^2 + \frac{2k^2 q^2 \sin^2 \theta}{3m^2 c^2} \right\} \right. \\ \left. - \frac{k^2}{2} \left\{ \frac{q^2 \cos^2 \theta}{m^2 c^2 + q^2} + \frac{2q^2 \sin^2 \theta}{3m^2 c^2} \left( 1 - \frac{1}{8(m^2 c^2 + q^2)} (3k^2 - 5k^2 \cos^2 \theta - 2k_0^2) \right) \right\} \frac{1}{(m^2 c^2 + q^2)^{\frac{1}{2}}} \right] d\mathbf{q} \quad (27b)$$

For  $r = 0$  the integrand in  $F_1^0$  decreases like  $q^{-3}$  for large values of  $q$  and therefore  $F_1^0$  diverges logarithmically, the terms in the integrand in  $F_1^1$  decrease either as  $q^{-3}$  or  $q^{-1}$  for large  $q$  and therefore  $F_1^1$  diverges both logarithmically and quadratically, while both in  $F_2^0$  and  $F_2^1$  integrands decrease with the higher order  $q^{-5}$  so that the total integrals given by (27a) and (27b) are convergent. If one identifies the subtractive terms with  $F_1^0(\mathbf{k}, k_0, \mathbf{r})$  and  $F_1^1(\mathbf{k}, k_0, \mathbf{r})$  given by (26a) and (26b) respectively, one then gets from (23a) and (23b) by putting the 'off diagonal distance',  $\mathbf{r}$ , equal to zero

$$\delta j_0^0 = -\frac{\alpha}{2\pi} f^0(\mathbf{k}, k_0) j_0 \quad (28a)$$

for the scalar meson theory, and

$$\delta j_0^1 = -\frac{3\alpha}{2\pi} f^1(\mathbf{k}, k_0) j_0 \quad (28b)$$

for the vector meson theory, where the functions  $f^0(\mathbf{k}, k_0)$  and  $f^1(\mathbf{k}, k_0)$  are given by (27a) and (27b) respectively. The expressions (28a) and (28b) may be considered as the induced charge densities in the two theories.

On evaluating the integrals (27a) and (27b) following the procedure of Pauli and Rose, we get

$$f^0(\mathbf{k}, k_0) = f(L) = -\frac{L}{3} \int_0^1 \frac{z^4 dz}{1 + L(1 - z^2)}, \quad (29a)$$

and

$$f^1(\mathbf{k}, k_0) = \left( 1 - \frac{4}{3} L \right) f(L), \quad (29b)$$

where

$$L = (k^2 - k_0^2)/4m^2 c^2. \quad (30)$$

It should be noticed that both  $f^0(\mathbf{k}, k_0)$  and  $f^1(\mathbf{k}, k_0)$  do not depend on  $k$  and  $k_0$  separately but on the single combination  $L$  which result is a consequence of the Lorentz invariance of the formalism.

$f(L)$  can be written in the form

$$f(L) = -\frac{1}{3} \left[ -\frac{4}{3} - \frac{1}{L} + \frac{(L+1)^2}{L} \phi(L) \right] \quad \dots \quad (31)$$

where

$$\phi(L) = \int_0^1 \frac{dz}{1+L(1-z^2)} \quad (32)$$

The evaluation of (32) is simple and the results given by Pauli and Rose are as follows

$$\phi(L) = [L(1+L)]^{-\frac{1}{2}} \log [(1+L)^{\frac{1}{2}} + L^{\frac{1}{2}}], \quad \text{for } L > 0, \quad (33a)$$

$$\phi(L) = [|L|(1-|L|)]^{-\frac{1}{2}} \sin^{-1} |L|^{\frac{1}{2}}, \quad \text{for } -1 < L < 0, \quad (33b)$$

$$\phi(L) = -[|L|(|L|-1)]^{-\frac{1}{2}} \log [(|L|-1)^{\frac{1}{2}} + |L|^{\frac{1}{2}}] \quad \text{for } L < -1 \quad (33c)$$

In the last case the integrand has a singularity at one point of the integration path, viz at  $z = \left( \frac{|L|-1}{|L|} \right)^{\frac{1}{2}}$ , and one has there to take the principal value

For large positive values of  $L$ , we get asymptotically

$$f^0(k, k_0) \cong \frac{4}{9} - \frac{1}{3} \log (2L^{\frac{1}{2}}), \quad (34a)$$

and

$$f^1(k, k_0) \cong \frac{4}{9} L \left[ -\frac{4}{3} + \log (2L^{\frac{1}{2}}) \right]. \quad (34b)$$

For  $|L| \ll 1$ , one get

$$f^0(k, k_0) = f^1(k, k_0) \cong -\frac{1}{15} L \quad \dots \quad (35)$$

In the case  $k_0 = 0$ , we have  $L = k^2/4m^2c^2$  and (29a), (29b), (31) and (33a) lead to the results

$$\begin{aligned} f^0(k^2) &= -\frac{k^2}{3} \int_0^1 \frac{z^4 dz}{4m^2c^2 + k^2(1-z^2)} \\ &= -\frac{1}{3} \left[ -\frac{4}{3} - \frac{4m^2c^2}{k^2} + \left(1 + \frac{4m^2c^2}{k^2}\right)^{\frac{1}{2}} \log \left\{ \left(1 + \frac{k^2}{4m^2c^2}\right)^{\frac{1}{2}} + \frac{k}{2mc} \right\} \right], \end{aligned} \quad (36a)$$

and

$$f^1(k^2) = \left(1 - \frac{k^2}{3m^2c^2}\right) f^0(k^2) \quad \dots \quad (36b)$$

When  $k^2 \ll m^2c^2$ , we get

$$f^0(k^2) = -\frac{1}{60} \frac{k^2}{m^2c^2} + \frac{1}{840} \frac{k^4}{m^4c^4} + \dots \quad (37a)$$

and

$$f^1(k^2) = -\frac{1}{60} \frac{k^2}{m^2c^2} + \frac{17}{2520} \frac{k^4}{m^4c^4} + \dots \quad (37b)$$

Hence from (28a) and (28b) one has

$$\delta j_0^0 = -\frac{\alpha}{2\pi} \left\{ \frac{1}{60} \left( \frac{\hbar}{mc} \right)^2 \nabla^2 j_0 + \frac{1}{840} \left( \frac{\hbar}{mc} \right)^4 \nabla^4 j_0 + \dots \right\} \quad \dots \quad (38a)$$

for the scalar meson theory, and

$$\delta j_0^1 = -\frac{3\alpha}{2\pi} \left\{ \frac{1}{60} \left( \frac{\hbar}{mc} \right)^2 \nabla^2 j_0 + \frac{17}{2520} \left( \frac{\hbar}{mc} \right)^4 \nabla^4 j_0 + \dots \right\} \quad \dots \quad (38b)$$

for the vector meson theory.

3 THE FUNCTION  $U(r)$ 

In our subsequent discussion we shall restrict ourselves to the time independent  $A_0$  and obtain an expression for the induced charge in a form given by Dr Uehling in the positron theory. In this case  $k_0 = 0$ , we have from (23a), (23b) and (28a), (28b) for the induced charge density

$$\delta j_0^0(\mathbf{r}') = -\frac{\alpha}{2\pi} \frac{k^2}{4\pi\hbar^2} A_0(\mathbf{r}') f^0(k^2) \quad (39a)$$

for the scalar meson theory, and

$$\delta j_0^1(\mathbf{r}') = -\frac{3\alpha}{2\pi} \frac{k^2}{4\pi\hbar^2} A_0(\mathbf{r}') f^1(k^2) \quad (39b)$$

for the vector meson theory, where  $f^0(k^2)$  and  $f^1(k^2)$  are given by (36a) and (36b) respectively. If now there be a continuous distribution of inducing charge  $j_0(\mathbf{r}'')$ , we have for the scalar potential

$$A_0(\mathbf{r}') = \int \frac{j_0(\mathbf{r}'') d\mathbf{r}''}{|\mathbf{r}' - \mathbf{r}''|} = \int A_0(\mathbf{r}') \exp -\frac{i}{\hbar} (\mathbf{r}' \mathbf{k}) d\mathbf{r}' = \frac{4\pi\hbar^2}{k^2} \int j_0(\mathbf{r}'') \exp -\frac{i}{\hbar} (\mathbf{r}'' \mathbf{k}) d\mathbf{r}'', \quad (40)$$

and for a single Fourier component with wave vector  $\mathbf{k}$

$$\begin{aligned} A_0(\mathbf{r}') &= \frac{4\pi\hbar^2}{V k^2} \int j_0(\mathbf{r}'') \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) d\mathbf{r}'' = -\frac{4\pi\hbar^4}{V k^4} \int j_0(\mathbf{r}'') \nabla^2 \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) d\mathbf{r}'' \\ &= \frac{4\pi\hbar^6}{V k^6} \int j_0(\mathbf{r}'') \nabla^4 \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) d\mathbf{r}'', \end{aligned} \quad (41)$$

where  $\mathbf{r} = \mathbf{r}' - \mathbf{r}''$ . On partial integration

$$A_0(\mathbf{r}') = -\frac{4\pi\hbar^4}{V k^2} \int \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) \nabla^2 j_0(\mathbf{r}'') d\mathbf{r}'' = \frac{4\pi\hbar^6}{V k^6} \int \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) \nabla^4 j_0(\mathbf{r}'') d\mathbf{r}'' \quad (42)$$

Hence combining all the Fourier components, we get from (39a)

$$\begin{aligned} \delta j_0^0(\mathbf{r}') &= \frac{\alpha}{2\pi} \frac{1}{8\pi^2\hbar} \int \int \frac{f^0(k^2)}{k^2} \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) \nabla^2 j_0(\mathbf{r}'') d\mathbf{r}'' d\mathbf{k} \\ &= \frac{\alpha}{8\pi^2} \int U^0(r) \nabla^2 j_0(\mathbf{r}'') d\mathbf{r}'' \end{aligned} \quad (43a)$$

for the scalar meson theory, where

$$U^0(r) = \frac{1}{2\pi^2\hbar} \int \frac{f^0(k^2)}{k^2} \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) d\mathbf{k} = \frac{2}{\pi} \int \frac{f^0(k^2)}{k^2} \frac{1}{r} \sin\left(\frac{kr}{\hbar}\right) k dk, \quad (44a)$$

and from (39b), (36b) and (42)

$$\begin{aligned} \delta j_0^1(\mathbf{r}') &= \frac{3\alpha}{8\pi^2} \int U^0(r) \left[ \nabla^2 j_0(\mathbf{r}'') + \frac{1}{3} \left(\frac{\hbar}{mc}\right)^2 \nabla^4 j_0(\mathbf{r}'') \right] d\mathbf{r}'' \\ &= \frac{3\alpha}{8\pi^2} \int \left[ U^0(r) + \frac{1}{3} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 U^0(r) \right] \nabla^2 j_0(\mathbf{r}'') d\mathbf{r}'' \\ &= \frac{3\alpha}{8\pi^2} \int U^1(r) \nabla^2 j_0(\mathbf{r}'') d\mathbf{r}'' \end{aligned} \quad (43b)$$

for the vector meson theory, where

$$U^1(r) = U^0(r) + \frac{1}{3} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 U^0(r) = \frac{1}{2\pi^2\hbar} \int \frac{f^1(k^2)}{k^2} \exp -\frac{i}{\hbar} (\mathbf{r} \mathbf{k}) d\mathbf{k} \quad (44b)$$

If we now substitute the integral (36a) for  $f^0(k^2)$  in (44a) we can integrate it following Pauli and Rose and have

$$U^0(r) = -\frac{1}{3r} \left[ \left( -\frac{2}{3}\xi^2 + 1 \right) K_0(2\xi) + \frac{4\xi}{3} (\xi^2 - 2) K_1(2\xi) + \xi \left( -\frac{4}{3}\xi^2 + 3 \right) B(2\xi) \right] \quad (45a)$$

where  $\xi = \frac{mc}{\hbar} r = \kappa r$ ,  $K_0(x)$  and  $K_1(x)$  are the well-known integrals for the Bessel functions of the second kind\*,

$$K_0(x) = \int_1^\infty \frac{e^{-qx}}{(q^2-1)^{\frac{1}{2}}} dq, \quad K_1(x) = x \int_1^\infty \frac{e^{-qx}}{(q^2-1)^{\frac{1}{2}}} dq$$

and  $B(x)$  is an indefinite integral of  $K_0(x)$

$$B(x) = \int_x^\infty K_0(y) dy = \int_1^\infty \frac{e^{-qx}}{q(q^2-1)^{\frac{1}{2}}} dq$$

Then from (44b) and (45a),  $U^1(r)$  is obtained as

$$U^1(r) = -\frac{1}{3r} \left[ -\frac{1}{3} (2\xi^2 + 1) K_0(2\xi) + \frac{2}{3\xi} (2\xi^4 + 1) K_1(2\xi) - \frac{\xi}{3} (4\xi^2 - 1) B(2\xi) \right] \quad (45b)$$

The function  $U^0(r)$  has a singularity at  $r = 0$  and decreases very rapidly to zero for values of  $r$  different from zero. The behaviour of the function  $U^1(r)$  is far worse at  $r = 0$ .

It can be shown that for small values of  $r$ , that is, for  $\xi \ll 1$  or  $r \ll \frac{\hbar}{mc}$

$$U^0(r) \sim \frac{1}{3r} \left[ \gamma + \log(\kappa r) + \frac{4}{3} + O(r) \right], \quad (46a)$$

and

$$U^1(r) \sim -\frac{1}{3r} \left[ \frac{1}{3\kappa^2 r^2} + \log(\kappa r) + \gamma - \frac{1}{3} + O(r) \right], \quad (46b)$$

where  $\gamma = 0.5772$  is the Euler's constant. We can also show that for large  $r$  ( $r \gg \frac{\hbar}{mc}$ )

$$U^0(r) \sim -\frac{\sqrt{\pi}}{8} \frac{1}{\kappa^{\frac{1}{2}} r^{\frac{1}{2}}} e^{-2\kappa r} [1 + O(r^{-1})], \quad (47a)$$

and

$$U^1(r) \sim -\frac{7\sqrt{\pi}}{24} \frac{1}{\kappa^{\frac{3}{2}} r^{\frac{3}{2}}} e^{-2\kappa r} [1 + O(r^{-1})] \quad (47b)$$

It should be noticed that both  $U^0(r)$  and  $U^1(r)$  tend to  $-\infty$  as  $r \rightarrow 0$ , and they approach the value zero from the negative side as  $r \rightarrow \infty$ .  $U^0(r)$  and  $U^1(r)$  are negative for all values of  $r$ , that is, whatever may be the values of  $r'$  and  $r''$ . Hence the sign of the induced charge is the same as the inducing one in both the theories in those regions of space where the sign of the Laplacian of the inducing charge is negative. Further if the Laplacian of the inducing charge exists in a certain region of space, the induced charge will exist in those regions and also in a small range of space of the order of the critical length  $\kappa^{-1}$  surrounding those regions. To get an approximate expression for the induced charge we expand  $\nabla^2 j_0(\mathbf{r}'')$  about the point  $\mathbf{r}'$  by Taylor's expansion and if the field is a slowly varying one we can retain only the first term in this expansion;

\* Watson, Theory of Bessel Functions, §6.3

then since the integral of  $U^0(r)$  or  $U^1(r)$  over all space is  $-\frac{\pi}{15} \left(\frac{\hbar}{mc}\right)^2$  we have from (43a) and (43b) as a first approximation

$$\delta j_0^0(\mathbf{r}') = -\frac{\alpha}{2\pi} \cdot \frac{1}{60} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 j_0(\mathbf{r}'),$$

and

$$\delta j_0^1(\mathbf{r}') = -\frac{3\alpha}{2\pi} \cdot \frac{1}{60} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 j_0(\mathbf{r}')$$

which are in agreement with the first term of (38a) and (38b) respectively

It is already seen that there exists an induced charge distribution in the immediate neighbourhood of space varying external charges. An immediate consequence of this corresponds to a new term in the mutual potential of the external charges when the charges are very close to one another within a distance of the order of the critical length. These forces will not in general be Coulomb forces and the deviations may be computed directly from (43a) and (43b). For point charges these deviations can be easily calculated from the interaction energy matrix, and this will be done in the next article.

#### 4 DEVIATION FROM THE COULOMB POTENTIAL

The interaction term associated with the scalar potential  $A_0(\mathbf{r}')$  is given by

$$H' = e \int A_0 \psi^* \beta_4 \psi d\mathbf{r}' = e \sum_{\mathbf{p}} \sum_{\mathbf{p}'} \{a^*(\mathbf{p})u^+(\mathbf{p})^* + b(\mathbf{p})u^-(\mathbf{p})^*\} \beta_4 \\ \times \{a(\mathbf{p}')u^+(\mathbf{p}') + b^*(\mathbf{p}')u^-(\mathbf{p}')\} \int A_0(\mathbf{r}') \exp \frac{i}{\hbar} (\mathbf{p}' - \mathbf{p}, \mathbf{r}') d\mathbf{r}' \quad (48)$$

Suppose there are two fixed point charges  $Z'e$  and  $Z''e$  at  $\mathbf{r}_1$  and  $\mathbf{r}_2$  separated by a distance  $r = |\mathbf{r}_2 - \mathbf{r}_1|$ . Under the influence of the mutual field of these charges pairs of mesons are created and annihilated. The total energy of the pair distribution can be obtained by using the perturbation matrix  $H'_{nk}$  for creation or annihilation of pairs as given by (48) from the expression

$$E' = \sum_n \sum_k \frac{|H'_{nk}|^2}{E_k - E_n} \quad (49)$$

One then obtains by the usual method

$$E' = -e^2 \sum_{\mathbf{p}} \sum_{\mathbf{p}'} \frac{\{u^+(\mathbf{p})^* \beta_4 u^-(\mathbf{p}')\} \{u^-(\mathbf{p}')^* \beta_4 u^+(\mathbf{p})\}}{E(\mathbf{p}) + E(\mathbf{p}')} \int A_0(\mathbf{r}') \exp \frac{i}{\hbar} (\mathbf{p}' - \mathbf{p}, \mathbf{r}') d\mathbf{r}' \\ \times \int A_0(\mathbf{r}'') \exp \frac{i}{\hbar} (\mathbf{p} - \mathbf{p}', \mathbf{r}'') d\mathbf{r}''$$

On summing over the directions of polarisation in the states  $\mathbf{p}$  and  $\mathbf{p}'$ , replacing the summations by integrations and defining  $\mathbf{p}' = \mathbf{q} + \mathbf{k}/2$  and  $\mathbf{p} = \mathbf{q} - \mathbf{k}/2$ , we get

$$E^0 = -\frac{e^2}{4c} \cdot \frac{1}{(2\pi\hbar)^3} \int A_0(\mathbf{r}') d\mathbf{r}' \int A_0(\mathbf{r}'') d\mathbf{r}'' \int d\mathbf{k} \exp -\frac{i}{\hbar} (\mathbf{k}, \mathbf{r}'' - \mathbf{r}') \int \frac{(\epsilon - \epsilon')^2}{\epsilon\epsilon'(\epsilon + \epsilon')} d\mathbf{q} \quad (50a)$$

for the scalar meson theory; and

$$E^1 = -\frac{3e^2}{4c} \cdot \frac{1}{(2\pi\hbar)^3} \int A_0(\mathbf{r}') d\mathbf{r}' \int A_0(\mathbf{r}'') d\mathbf{r}'' \int d\mathbf{k} \exp -\frac{i}{\hbar} (\mathbf{k}, \mathbf{r}'' - \mathbf{r}') \int \frac{1}{\epsilon\epsilon'(\epsilon + \epsilon')} \\ \times \left\{ (\epsilon - \epsilon')^2 + \frac{2}{3m^2c^2} (q^2 k^2 - (\mathbf{q}\mathbf{k})^2) \right\} d\mathbf{q} \quad (50b)$$

for the vector meson theory, where  $\epsilon$  and  $\epsilon'$  are defined by (22). After subtraction of the singularities as before, (50a) and (50b) assume the forms

$$E^0 = -\frac{\alpha}{128\hbar^5\pi^5} \int A_0(\mathbf{r}') d\mathbf{r}' \int A_0(\mathbf{r}'') d\mathbf{r}'' \int k^2 d\mathbf{k} f^0(k^2) \exp -\frac{i}{\hbar} (\mathbf{k}, \mathbf{r}'' - \mathbf{r}'), \quad (51a)$$

and

$$E^1 = -\frac{3\alpha}{128\hbar^5\pi^5} \int A_0(\mathbf{r}') d\mathbf{r}' \int A_0(\mathbf{r}'') d\mathbf{r}'' \int k^2 d\mathbf{k} f^1(k^2) \exp -\frac{i}{\hbar} (\mathbf{k}, \mathbf{r}'' - \mathbf{r}'), \quad (51b)$$

where  $f^0(k^2)$  and  $f^1(k^2)$  are given by (36a) and (36b) respectively. If we now introduce the potential we have from (40)

$$\begin{aligned} \int A_0(\mathbf{r}') \exp \frac{i}{\hbar} (\mathbf{k}\mathbf{r}') d\mathbf{r}' &= \frac{4\pi\hbar^2 e}{k^2} \left[ Z' \exp \frac{i}{\hbar} (\mathbf{k}\mathbf{r}_1) + Z'' \exp \frac{i}{\hbar} (\mathbf{k}\mathbf{r}_2) \right], \\ \int A_0(\mathbf{r}'') \exp -\frac{i}{\hbar} (\mathbf{k}\mathbf{r}'') d\mathbf{r}'' &= \frac{4\pi\hbar^2 e}{k^2} \left[ Z' \exp -\frac{i}{\hbar} (\mathbf{k}\mathbf{r}_1) + Z'' \exp -\frac{i}{\hbar} (\mathbf{k}\mathbf{r}_2) \right] \end{aligned}$$

On substitution of these quantities in (51a) and (51b), the terms depending on  $Z'^2$  and  $Z''^2$  alone represent the contribution to the proper energy of the charges, and the product term represents the interaction energy. We then get

$$E_{\text{int}}^0 = -\frac{\alpha Z' Z'' e^2}{4\hbar\pi^3} \int \frac{f^0(k^2)}{k^2} \exp -\frac{i}{\hbar} (\mathbf{k}\mathbf{r}) d\mathbf{k} = -\frac{\alpha Z' Z'' e^2}{2\pi} U^0(r), \quad (52a)$$

and

$$E_{\text{int}}^1 = -\frac{3\alpha Z' Z'' e^2}{4\hbar\pi^3} \int \frac{f^1(k^2)}{k^2} \exp -\frac{i}{\hbar} (\mathbf{k}\mathbf{r}) d\mathbf{k} = -\frac{3\alpha Z' Z'' e^2}{2\pi} U^1(r), \quad (52b)$$

where  $U^0(r)$  and  $U^1(r)$  are defined by (44a) and (44b). Thus the mutual potential energy of two fixed point charges  $Z'e$  and  $Z''e$  separated by a distance  $r$  is

$$V^0(r) = Z' Z'' e^2 \left[ \frac{1}{r} - \frac{\alpha}{2\pi} U^0(r) \right] \quad (53a)$$

for the scalar meson theory, and

$$V^1(r) = Z' Z'' e^2 \left[ \frac{1}{r} - \frac{3\alpha}{2\pi} U^1(r) \right] \quad (53b)$$

for the vector meson theory. Since  $U^0(r)$  and  $U^1(r)$  are negative for all values of  $r$ , the deviation from Coulomb law is always positive for like charges in both the theories.

## 5. ELASTIC SCATTERING OF HEAVY PARTICLES.

When the distance of separation is of the order of the critical length  $\kappa^{-1}$ , the deviations from Coulomb field discussed in the previous article become effective and may perhaps be detected by scattering experiments. It has already been pointed out that all the calculations of the present theory are based on the assumption that the field strength should always be small compared to the critical field. If the charge on the particles is not greater than  $Ze$  then the condition  $|\mathbf{E}| < \frac{m^2 c^3}{\hbar e}$  means only that the distance

of separation of particles must be greater than  $(\alpha Z)^{\frac{1}{2}} \kappa^{-1}$ . Hence in order that our calculations may be within the range of the validity of the theory the energy of the incident particle should be assumed to be such that the distance of closest approach is greater than this distance. On this supposition the deviations from the scattering for a Coulomb field are to be found in the present section.

Since the deviations from ordinary Coulomb scattering will be important only for high energetic incident particles the Born's approximation may be used. According to Born's theory the scattered amplitude for unit incident flux scattered by a fixed scattering centre is

$$\chi(\theta) = -\frac{M}{2\pi\hbar^2} \int V(r) \exp \frac{ip}{\hbar} (\mathbf{e} - \mathbf{n}, \mathbf{r}) d\mathbf{r}, \quad \dots \quad (54)$$

where  $\mathbf{e}$  is the unit vector in the direction of incident particle,  $\mathbf{n}$  is the unit vector in the direction in which scattering is observed,  $\theta$  is the angle between  $\mathbf{e}$  and  $\mathbf{n}$ ,  $p$  is the initial momentum and  $M$  is the mass of the incident particle. If  $Z'e$  and  $Z''e$  be the charges of the incident and scattering particles, then the mutual potential energy  $V(r)$  is given by (53a) in the scalar meson theory and by (53b) in the vector meson theory,  $V(r)$  being the Coulomb potential plus the deviation from it. On evaluation of the integral (54) we get

$$\chi^0(\theta) = -\frac{MZ'Z''e^2}{2p^2} \operatorname{cosec}^2 \frac{\theta}{2} \left[ 1 + \frac{\alpha}{8\pi} G^0(l) \right] \quad (55a)$$

for the scalar meson theory, and

$$\chi^1(\theta) = -\frac{MZ'Z''e^2}{2p^2} \operatorname{cosec}^2 \frac{\theta}{2} \left[ 1 + \frac{\alpha}{2\pi} G^1(l) \right] \quad (55b)$$

for the vector meson theory, where

$$G^0(l) = -3f^0(l) = l^2 \int_0^1 \frac{z^4 dz}{4 + l^2(1-z^2)} = -\frac{4}{3} - \frac{4}{l^2} + \left(1 + \frac{4}{l^2}\right) \log \left\{ \left(1 + \frac{l^2}{4}\right)^{\frac{1}{2}} + \frac{l}{2} \right\}, \quad (56a)$$

$$G^1(l) = -3f^1(l) = \left(1 - \frac{l^2}{3}\right) G^0(l), \quad \dots \quad (56b)$$

$$l = \frac{2p}{mc} \sin \frac{\theta}{2}, \quad \dots \quad (57)$$

where  $m$  is the mass of the meson. The first term in (55a) or (55b) gives the ordinary Coulomb scattering and the second term is the contribution to the deviation from this scattering law. For small values of  $l$

$$G^0(l) \sim G^1(l) \sim \frac{l^2}{20}, \quad \dots \quad (58)$$

and for large  $l$

$$G^0(l) \sim -\frac{4}{3} + \log l, \quad \text{and} \quad G^1(l) \sim -\frac{l^2}{3} \left( -\frac{4}{3} + \log l \right) \quad \dots \quad (59)$$

Hence for small values of  $l$ , the deviation from the Coulomb scattering is finite and small for all values of  $\theta$  in both the theories. The function  $G^0(l)$  has no real zeros, while the function  $G^1(l)$  has only one real zero at  $l = \sqrt{3}$ . For particles of a given incident velocity the function  $G^0(l)$  of the scalar meson theory rises rapidly with increasing  $\theta$  in the neighbourhood of  $\theta = 0$  and then assumes practically constant value increasing with  $\theta$  as logarithm of  $\sin \theta/2$  throughout the major portion of the angular range. On the other hand for particles of given incident velocity the function  $G^1(l)$  of the vector meson theory rises rapidly with increasing  $\theta$  in the neighbourhood of  $\theta = 0$  and remains positive up to the value of  $\theta$  for which  $l = \sqrt{3}$  at which it attains the zero value, and afterwards it becomes negative, the absolute value increasing rapidly with  $\theta$  practically as quadratic function of  $\sin \theta/2$  for the rest of the portion of angular range. Thus according to the scalar meson theory the deviation from ordinary scattering law is practically constant and has a small magnitude, and so it has very little chance of experimental detection; but this effect as obtained from the vector meson theory may perhaps be detected by experiment. It must again be pointed out that for very close distance of approach which is possible when the energy of the incident particle is very high, where these deviations may be large, the theory may not be applied.

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## VARIATION IN THE RATE OF GROWTH IN PLANTS

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(Communicated by Prof S P Agharkar, M A , Ph D , F.L.S , F N I )

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Extensive work has been done on the growth of plants. An old reference on this subject happens to be the observations of Sachs (1873), who has selected increase in length to explain the rate of growth. While many have studied the rate of elongation for determining the rate of growth others have selected either the leaf area or the dry weight of the plant or both for this investigation. Gregory (1921) studied the length, breadth and area of leaves of some plants and hinted that the rate of growth satisfied the 'Compound interest law' of Blackman (1919). Briggs, Kidd and West (1920a, 1920b) have analysed the growth of maize plant in terms of dry weight and leaf area, and explained the weekly increase in the plant. Miller's work (1925) is also in the same direction. Numerous attempts have been made to give a mathematical expression to explain the rate of growth. Blackman (1919, 1920), Robertson (1923), Copeman (1928) and Gregory (1928) are some of the people who advanced equations. Most of these equations are based on the assumption that the average rate of growth for a particular plant is constant.

Several investigators have tried to explain the periodic fluctuations in the growth. Sachs (1873) mentions about the daily 'rhythm' in the growth rate of plants, thus indicating a single curve in the course of 24 hours. But Friesner's (1920) observations on the radicles of *Cucurbita* and other plants point out that instead of a single curve there will be 2-4 curves or oscillations in the rate in the course of a day. He mentions that even under artificial illumination and constant external conditions a similar feature is manifested and suggests that a distinction should be made between 'Periodicity' and 'Rhythm', the latter, according to him, denoting the oscillations definite and regular and not related to any external influence. Thus the word 'rhythm' used by Sachs is actually periodicity. Since growth is the result of several metabolic processes in plants, fluctuations in these may result in the variations in the rate of the former. The author's reinvestigation of the several activities (Krishna Iyengar, 1942 a, b; 1943 a, b, c) indicate that there are variations in the rates of all these even under constant conditions. A preliminary note on the growth of the coleoptile of *Zea Mays* was published by the author (Krishna Iyengar, 1942c) some time ago, to explain as briefly as possible the occurrence of these oscillations in the rate at short intervals. The author's observations on the rate of elongation in some plants form the subject matter of the present paper.

### MATERIALS AND METHODS.

The radicle of *Dolichos Lablab*, coleoptile of *Zea Mays*, petiole of *Colocasia* sp., leaf of *Allium Cepa*, peduncle of a species of *Begonia* and the flower bud of *Lilium* sp. are selected for the present paper. These were studied under constant artificial illumination. The plants were left in the room for several hours before recording was started. The room temperature varied from day to day ranging from 74° to 76° F, but during the short periods of observation the temperature as also percentage of atmospheric humidity remained constant. An optical lever was employed to record growth, and the magnification made use of was between 2000 and 3000. The time interval of the readings happened to be  $\frac{1}{2}$  minute for the coleoptile and  $\frac{1}{4}$  minute for the rest. The records are mostly of 10 to 15 minutes duration. Nutation effects were found to be almost nil during the short periods of observation. Control experiments were performed on dead material employing a similar magnification. There was no change in the position of the

lever While drawing the graphs the rates obtained are magnified four times to enable proper reproduction of the figures after reduction.

#### OBSERVATIONS

Fig. 1 shows the rate of elongation of the radicle of *Dolichos* at intervals of  $\frac{1}{4}$  minute. The alternating peaks and hollows indicate the fluctuations in the rate from time to time. When the major peaks are taken into account it may be stated that these appear at

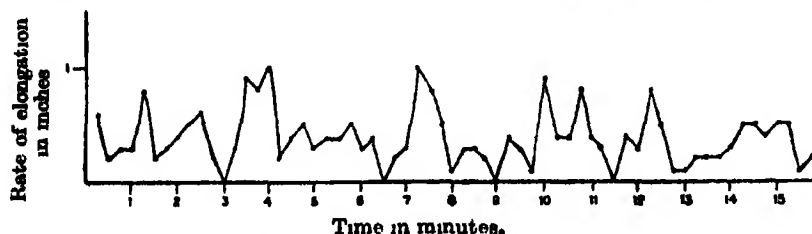


FIG. 1 Graph showing the rate of elongation in the radicle of *Dolichos Lablab*  $\times 8000$ .

intervals of 2–4 minutes and represent very high rate of elongation. If the minor peaks are also considered then it is noticed that the fluctuations in the rate of growth occur at short intervals of  $\frac{1}{4}$  to 2 minutes.

The next figure (Fig. 2) is that of the coleoptile of *Zea Mays* and shows two graphs A and B, the former indicating the growth curve and the latter explaining the rate of elongation at intervals of 10 seconds. The growth curve (A) shows series of undulations

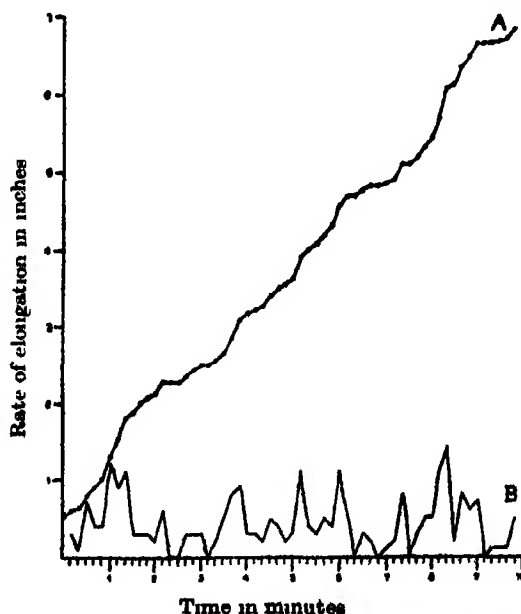


FIG. 2 Graph showing the growth curve (A) and the rate of elongation (B) in the coleoptile of *Zea Mays* (a)  $\times 3000$ . (b)  $\times 12000$

although the external conditions were maintained constant. There are significant fluctuations or oscillations in Graph B, and their number happens to be quite large. The time interval between successive oscillations happens to be  $\frac{1}{4}$  to 1 minute or slightly more.

The rate of elongation of the petiole of *Colocasia* sp is shown in Fig 3. The graph indicates that the growth rate is rarely steady, but is often given to a series of fluctuations

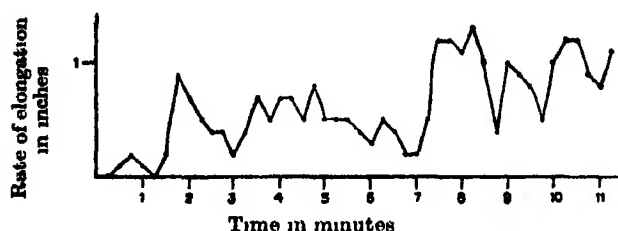


FIG 3 Graph showing the rate of elongation in the petiole of *Colocasia* sp  $\times 8000$

even at very short intervals. The frequency of these fluctuations or oscillations in the rate may be taken to be the same as before. The next figure (Fig 4) is that of the leaf of *Allium Cepa*, the recording of which is at  $\frac{1}{2}$  minute intervals. The graph shows significant fluctuations in the rate of elongation. The time interval between the successive

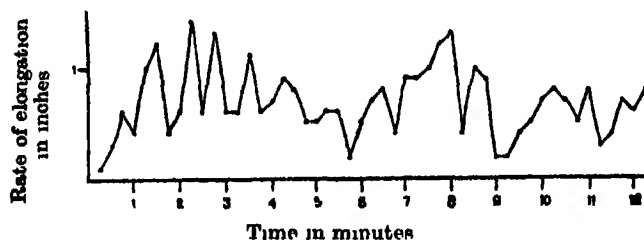


FIG 4 Graph showing the rate of elongation in the leaf of *Allium Cepa*  $\times 8000$

oscillations seems to be  $\frac{1}{2}$  to 1 minute or more. Although the period of observation is short there are three pronounced periods of growth the first two being over by about the end of the 6th and 9th minutes respectively, indicating thereby that a high rate of activity goes on only for a few minutes and that this is followed by one of reduced rate. There are altogether 13 oscillations in the course of 12 minutes, some occurring at intervals of  $\frac{1}{2}$  minute, others taking a minute or more.

Since the rate of elongation was appreciable the peduncle of *Begonia* species was next selected to explain the variation in the rate (see Fig 5). The readings are at intervals

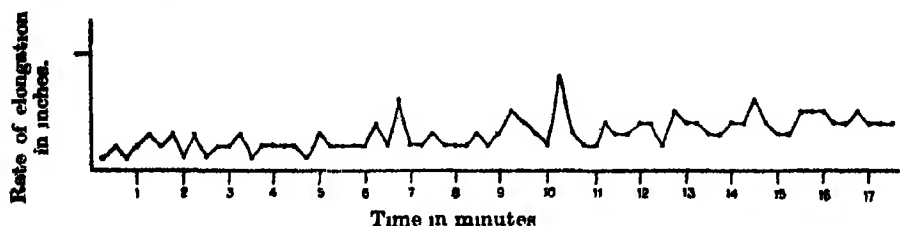


FIG 5 Graph showing the rate of elongation in the peduncle of *Begonia* sp  $\times 8000$

of  $\frac{1}{2}$  minute. The graph shows not only the frequency of oscillations but also the significant difference between the maximum and minimum rates of elongation. Fig 6 shows the rate of elongation of the flower bud of *Lilium* sp. The pedicel did not show appreciable linear changes during the elongation of the bud, although the growth was watched from day to day. Thus the record presented may be taken to represent only the rate

of elongation of the perianth lobes. During certain periods the growth rate is negligible while at other times this is highly pronounced. The number of smaller and larger oscilla-

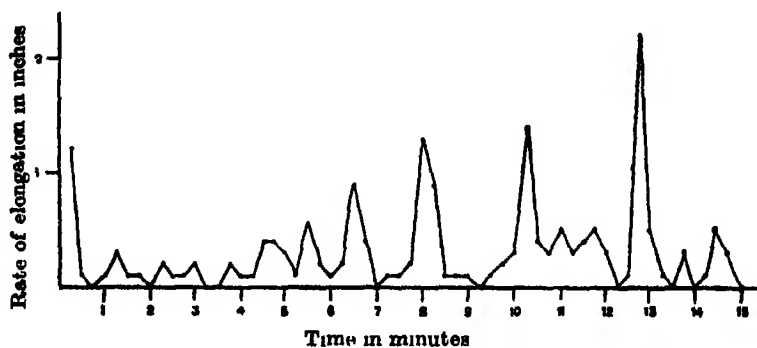


FIG. 6 Graph showing the rate of elongation in the flower bud of *Lulium* sp.  $\times 8000$

tions is 15 during a period of about 15 minutes showing an average of one oscillation per minute, although the time interval between the successive oscillations may be taken to be generally between  $\frac{1}{2}$  to 2 minutes.

#### CONCLUSION

The above observations indicate that the rate of elongation is made up of a series of fluctuations instead of being uniform. Whether the readings are taken at intervals of  $\frac{1}{2}$ ,  $\frac{1}{4}$ , 1 minute or more there are oscillations in the growth, the most significant variations in the rate being, however, noticed when the recording interval is less than a minute. The oscillations occurring at intervals of  $\frac{1}{2}$  to 1 minute or slightly more will be missed when readings are taken at minute intervals. Similarly the oscillations at intervals of 2 to 5 minutes or 10 to 15 minutes may be lost when the recording interval is proportionately longer. This has been explained by the author in his paper on the autonomic movements of leaves (Krishna Iyengar 1942b). It is also noticed that a period of high rate of activity is always followed by one of depressed rate, these indicated by the oscillations. Friesner (1920) mentions about 2 to 4 oscillations in the rate of growth during a period of 24 hours, the time interval between successive oscillations thus being several hours. But the present observations indicate that there are oscillations appearing at even shorter intervals, some appearing at intervals of  $\frac{1}{2}$  to 1 or 2 minutes, while others appear at intervals of 2 to 5 minutes and 10 to 20 minutes or more. According to the author the oscillations (at intervals of a few hours) as explained by Friesner are the result of long interval readings and that these ought to be composed of a series of oscillations at shorter intervals, the long interval between the successive readings being responsible for the absence of the several kinds of oscillations. The author has already explained in his previous papers (Krishna Iyengar 1942b, 1943b) the importance of short interval readings in studying the various activities of plants. A diagrammatic representation of the oscillations (Fig. 7) is given below to explain the different types of oscillations and their relationship. The manifestation of the different kinds of oscillations seems to be the characteristic feature of many activities of plants. According to the author each primary oscillation taking several hours is composed of several secondary oscillations at intervals ranging from 10 to 20 or 25 minutes, the latter in their turn made up of tertiary oscillations at intervals of 2 to 5 minutes, while the third kind is composed of a series of oscillations at shorter time-intervals ( $\frac{1}{2}$  to 1 or 2 minutes). The four kinds of oscillations may be styled as the oscillations of the first, second, third and fourth orders. All these appear even when the external conditions are constant and indicate the existence of a rhythm in the activity.

There are several external and internal factors affecting the rate of growth, but a detailed enquiry into the former is unnecessary since the conditions were maintained

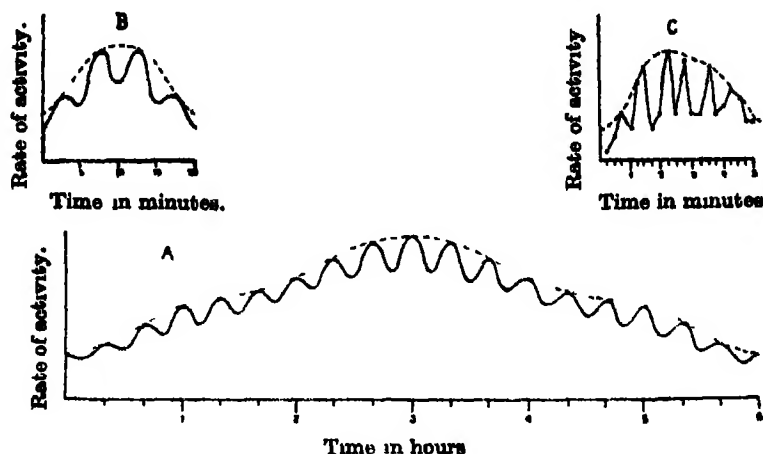


FIG 7 A diagrammatic representation of the several types of oscillations and their relationship (A) Primary oscillation (dotted line) and Secondary oscillations (bold line) (B) Secondary oscillation (dotted line) and Tertiary oscillations (bold line) (C) Tertiary oscillation (dotted line) and Momentary oscillations (bold line) (Part of Fig 4)

constant during the brief periods of observation. However, a mention of the work of Silberschmidt (1926) and Went (1925) may not be out of place. Silberschmidt has studied the effect of temperature on the growth rate of the coleoptiles of *Avena* and *Triticum* and recorded growth at intervals of 5 minutes. The data show that there are significant fluctuations in the rate generally at intervals of 10 to 20 minutes even though the temperature happens to be constant for a long period, but this feature has escaped the notice of the author. Similarly, Went's work on the *Avena* coleoptile indicates fluctuations in the rate of growth from time to time, even when the illumination remains constant. It is strange that both the investigators should have failed to notice this feature although in both cases the recording is at short intervals.

Water-content of the plant body is an important factor deciding the rate of growth. According to Sachs (1873) considerable turgor pressure in the cells by the absorption of water results in a very high rate of elongation, and any fluctuation in the former necessarily results in the variation of the latter. The author's observations on the leaf movements and the fluctuating weight of plants (Krishna Iyengar, 1942b, 1943 b, c) indicate that the turgidity of the plant body will be varying from time to time, the balance of water-content being either positive or negative, thus affecting the turgor pressure in the cells. A similar feature in the present members probably accounts for the noticed variations in the rate of growth. The 'rhythmic change' in the potential in the plant body at short intervals and the 'pulsating nature' of the growing organs as explained by Bose (1923, 1927) go to confirm the author's idea of the existence of a rhythm in the fluctuation of the water-content of the plant.

An equally important factor determining the rate of growth happens to be the action of the growth hormones. Boysen-Jensen (1910), Went (1928), Heyn (1931) and many others have emphasised the importance of this factor. The data of Heyn (1931) indicate a variation in the rate of growth of *Avena* coleoptile even though the recording is at  $\frac{1}{4}$  hour interval. Just like Silberschmidt and Went even Heyn has failed to notice this feature. Although the hormonal action is catalytic still the number of units and the tone of the hormones acting at a particular place may decide the rate of growth. Since the hormones are intimately associated with the protoplasm any variation in the tone of the latter due to the several metabolic activities will necessarily result in the variation

in the rate of hormone production and the intensity of its action, with an immediate effect on the rate of growth. Thus, it seems highly probable that the production and activity of the hormones are also open to fluctuations, if one can judge from the significant fluctuations in the rate of growth. In conclusion it may be stated that growth is as much open to periodic and rhythmic fluctuations as several other activities of the plants (Krishna Iyengar, 1942 a, b, 1943 a, b, c)

#### SUMMARY

The radicles of *Dolichos Lablab*, Coleoptile of *Zea Mays*, petiole of *Colocasia* sp, leaves of *Allium Cepa*, peduncle of *Begonia* sp and the flower bud of *Lilium* sp were selected for investigating the rate of elongation.

The plants were studied under artificial illumination and constant room temperatures and humidity. Readings were taken at intervals of  $\frac{1}{4}$ ,  $\frac{1}{2}$  or 1 minute according to the needs, and the magnification employed was between 2,000 and 3,000.

The graphs represented indicate that the rate of elongation is rarely constant and that this is given to a series of fluctuations at short and long intervals.

The fluctuations or oscillations in the rate appear not only at intervals of a few hours but also at short intervals of 10 to 20 minutes, 2 to 5 minutes and even  $\frac{1}{2}$  to 1 or 2 minutes, indicating thereby the existence of a rhythm in this activity.

Variation in the water-content of the plant body from time to time and constantly changing tone of the protoplasm (due to several metabolic activities) with the consequent fluctuation in the rate of action of the growth hormones seem to be directly connected with the noticed oscillations in the growth rate.

The author expresses his indebtedness to Dr S. P. Agharkar, M A., Ph D, F L S, F.N I., of Calcutta University for his kind encouragement.

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## Nineteenth Ordinary General Meeting.

The Nineteenth Ordinary General Meeting of the National Institute of Sciences of India was held at 5-30 P M on Friday, the 27th August, 1943, in the hall of the Royal Asiatic Society of Bengal, 1 Park Street, Calcutta

### Present —

Prof. S K Mitra, *Vice-President*, in the Chair  
Rai Bahadur Dr K N Bagechi, *Honorary Treasurer*  
Rai Bahadur Dr S. I. Hora, *Editor of Publications*  
Dr K Banerjee  
Dr J A Dunn  
Prof B C Guha  
Dr. A C Joshi  
Prof P Ray  
Prof M N Saha  
Dr S C Sirkar  
Prof. S P Agharkar } *Honorary Secretaries*  
Sir Cyril S Fox }

1 The minutes of the Eighth Annual General Meeting, held on the 1st January, 1943, were read and confirmed

2 Dr S C Sirkar signed the duplicate obligation and was admitted as a Fellow as per Rule 13 of the Rules of the Institute

3 The following papers were read.—

(1) Structure and development of the ovule and embryo sac of *Piper longum* L  
By Dr A C Joshi

(2) Excitation processes of the Night Spectrum By Mr S N Ghosh (Communicated by Prof S K Mitra)

4 In the absence of authors the following papers were taken as read —

(1) The Spermatogenesis of *Ichthyophis glutinosus* Linn Part 3 Spermateliosis  
By Dr B R Seshachar (Communicated by Dr B Prashad.)

(2) On a new Coccidium, *Eimeria himalayanum* N Sp from the intestine of a Himalayan toad, *Bufo himalayanus* Boulenger By Dr H N Ray and Mr. P L Misra (Communicated by Dr B Prashad)

(3) Studies in the family Alismaceae V The Embryology of *Machaerocarpus californicus* (Torr) Small By Dr P Maheshwari and Mr Balwant Singh

(4) Thermodynamics of a Fermi-Diarc gas obeying Born's modified Quantum Statistics By Messrs Brij Nath and F C Auluck (Communicated by Dr D S Kothari)

(5) On the finger nails and nail phalanx of twins By Mr S S Sarkar (Communicated by Dr D M Bose)

(6) The effect of screening on the Bremsstrahlung and pair creation processes and its consequence on the Cascade Theory By Mr S K Chakrabarty (Communicated by Prof H J Bhabha)

(7) Variation in the growth of Plants By Mr C V Krishna Iyengar (Communicated by Prof S P Agharkar)

(8) Polarisation of the vacuum in the Meson Theory By Mr S Gupta (Communicated by Prof N R. Sen)

(9) On some Archiannelids of the Madras Coast. By Prof R. Gopala Aiyar and Mr. K H. Alukunhi.

With a vote of thanks to the chair the meeting terminated



## Twentieth Ordinary General Meeting.

The Twentieth Ordinary General Meeting of the National Institute of Sciences of India was held on the 27th and 28th September, 1943, in the hall of the Royal Asiatic Society of Bengal, 1 Park Street, Calcutta, in which a Symposium on 'Post-war organisation of Scientific Research in India' was held

The following Fellows of the Institute were present —

Sir Jnan Chandra Ghosh, <i>President</i> , in the Chair.	
Prof S K Mitra, <i>Vice President</i>	
Rai Bahadur Dr K N Bagchi, <i>Honorary Treasurer</i>	
Prof J N Mukherjee, <i>Foreign Secretary</i>	
Rai Bahadur Dr S L Hora, <i>Editor of Publications</i>	
Sir S S Bhatnagar	Prof. P C Mahalanobis
Prof K Banerjee	Prof P C Mitter
Prof S R Bose	Dr K G Naik
Dr J A. Dunn	Dr. C W B Normand
Dr B N Ghosh	Prof P Ray.
Prof J Ghosh	Prof M N Saha
Dr P K Ghosh	Dr P B Sarkar
Prof B C Guha	Mr B M Sen
Dr M Ishaq	Dr H K Sen
Dr K V Krishnan	Principal J M Sen
Dr R B Lal	Dr A C Ukil
Prof S P Agharkar, <i>Honorary Secretary</i>	

About 50 visitors, including representatives of science departments and delegates of learned societies, were present and took part

The Hon'ble Sir Azizul Haque, Member of Council for Commerce, Government of India, inaugurated the Symposium

He was followed by the President, Sir Jnan Chandra Ghosh. Papers were read in which the general principles underlying the planning and co-ordination of scientific research and the constitution of the organisations for the purpose as developed in the leading nations of the world were explained, account was given of the work done by the various research institutions in India (Government Departments, Universities and other unattached institutions) and attention was drawn to the problems facing post-war India. The following gentlemen participated in the discussion —

Sir J C Ghosh, Dr K G Naik, Prof M N Saha, Sir S S Bhatnagar, Dr J de Graaf Hunter, Dr C W B Normand, Prof J N Mukherjee, Rai Bahadur S L Hora, Prof S K Mitra, Prof B C Guha, Dr J A Dunn, Prof P C Mahalanobis, Dr H K Sen and Prof S P Agharkar

Papers were also received for discussion from Dr J B Grant, Sir Cyril Fox, Sir John Taylor, Prof H J Bhabha, Dr D. M. Bose, Prof V. Subrahmanyam, Lt -Col S S Sokhey and Rao Bahadur B Viswanath

After the reading of papers, proposals for the constitution of a National Research Council were discussed and the following resolutions were adopted —

I The Council of the National Institute of Sciences of India be authorised to take necessary steps for the organisation of a National Research Council constituted under the statutory authority of the Government of India. The National Research Council shall be directly responsible to the Government and have the following functions —

- (a) To plan the main lines of scientific work in accordance with national needs, to formulate schemes for the above purpose, to review and modify the same whenever necessary and to recommend ways and means for implementing the results of accomplished researches
- (b) To ensure balanced development of all branches of Science, and minimise overlapping

- (c) To advise and help relevant authorities regarding the training and supply of scientific personnel for pure and applied research

### CONSTITUTION.

#### *National Research Council*

The National Research Council shall consist of scientific and technical experts not exceeding 60 in number, the majority of whom shall be elected by non-official scientific organisations, including Universities and institutions of University rank, the remaining number being nominated by the Government of India from among the scientific and technical experts. The President of the National Research Council shall be nominated by the Government of India from among the members. A Vice-President shall be elected by the National Research Council from among its members. A whole-time salaried Secretary shall be appointed by the National Research Council for carrying on its work, who will not be a member of the Council.

#### *Governing Body of the National Research Council*

There shall be a Governing Body of the National Research Council which shall consist of the following —

The President and Vice-President of the National Research Council and the Chairman and Vice-Chairman of each of the Boards.

#### *Boards of Research*

For the performance of its functions the National Research Council shall constitute the following Boards of Research from among its own members, each of which will be responsible, within its own particular sphere, for giving effect to the policy of the National Research Council

- 1 Board of Scientific Research,
- 2 Board of Agricultural Research (Soils, Crops and Animal Husbandry),
- 3 Board of Medical and Public Health Research,
- 4 Board of Engineering Research,

and such other Boards as may be considered to be necessary.

The maximum number of members of each of the Boards of Research shall be 50. The National Research Council shall appoint the Chairman and Vice-Chairman for each Board and shall co-opt eminent scientific workers in different branches in consultation with non-official scientific organisations, Universities and institutions of University rank, scientific departments of the Government and Federations of Chambers of Commerce.

#### *Research Committees*

For the performance of its work, each Board will be authorised to constitute Research Committees for all important subjects, to settle the objectives of research, indicate the individuals or organisations which could undertake the several component parts of the enquiry, receive and co-ordinate the resulting information, make it available to those who will turn it to advantage and to form a national plan into which all who are in a position to contribute information can fit the particular lines of research. Governing Bodies of National Research laboratories, when established, shall be constituted in consultation with the relevant Research Committees.

II The Government of India be requested to form development corporations for the performance of functions analogous to those performed by the Research Enterprises Ltd. in Canada. The National Research Council shall be represented on the Governing Bodies of the development corporations.

III. To enable effect being given to the policy of scientific development determined by the National Research Council, the Government of India should make an annual grant of five crores of rupees per annum

It was resolved further that these proposals be circulated to the Government Scientific Departments, Universities, learned societies and unattached institutions for expression of their views, and discussed, with a view to their being given effect to, at another Symposium meeting to be held at Delhi towards the end of the year at which representatives of the relevant organisations would be invited to be present.

Fellows and visitors were entertained at a tea party given by the President and Calcutta Members of Council of the Institute

With a vote of thanks to the chair the meeting terminated.



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